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Heat Release From Forest Fuels Final

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FINAL REPORT SUBMITTED TO THE FOREST SERVICE

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ABSTRACT

The temperature dependence of heat release from forest fuels is determined by thermal evolution analysis (TEA). Heat release profiles of several natural fuels have been developed which can be incorporated into fire spread models and related to the ignition and combustion characteristics of the fuels. Particular attention is given to the heat content of the extractives and their heat release as a function of temperature. The fuel samples exhibit a wide variation in extractive contents, and the contribution of the extractives to the heat available to initiate or sustain combustion varies accordingly, from 14 to 61 percent. The evolution of heat due to the extractives continues throughout the temperature range studied. Gas-liquid chromatography of the low-temperature volatile products has shown that these compounds are not entirely associated with the extractive fractions and should, therefore, be identified and studied individually.

I. INTRODUCTION

Fire spread involves generation of combustible volatile products by continuous heating and pyrolysis of the unburned fuel and ignition of the volatile products evolved. In this process the unburned fuel must receive enough energy from its environment to reach the ignition temperature, where the combustion of the volatile products provides the energy necessary to bring additional fuel elements to ignition. The temperature at which the fuel/air mixture required for ignition is acheived could vary considerably depending on the fuel chemistry. The fraction of the total heat content of a fuel released in the gas phase combustion, the "effective heat content", is important in sustaining combustion, whereas the temperature dependence of the heat release determines the ease of ignition of additional fuel elements. Both of these parameters affect the rate of flame spread and must be accounted for in fire models such as the Forest Service model developed by Rothermel.[1]

The direction of this study is focused on the extractives because they are important both in terms of ignitibility and their contribution to the effective heat content. The cell wall components, such as the polysaccharides and lignin contribute to the flaming combustion only after thermal degradation at high temperatures, with much of their heat content remaining in the char. The extractives, however, could evaporate at low temperatures making all of their heat content available to the gas phase combustion or providing adequate fuel/air mixtures for ignition at relatively low temperatures.

The Wood Chemistry Laboratory of the University of Montana, under a previous cooperative agreement with the Northern Forest Fire Laboratory has determined the effective heat content of dead forest fuels.[2] The current

study is an extension of that work to the determination of the heat release as a function of temperature using living fuel samples. Through analysis of extracted and unextracted fuels, the thermal characteristics of the extractives can be established and related to the ignitibility and combustibility of the fuels.

II. EXPERIMENTAL PROCEDURES

A. SAMPLES

All samples were supplied by the Northern Forest Fire Laboratory. Upon receipt at the Wood Chemistry Laboratory the green foliage samples were freeze-dried for twelve hours, then ground in a Wiley mill. The 40-80 mesh fraction was used for the subsequent analyses. The gas-liquid chromatography (GLC) analysis, described in paragraph G, did not show any significant change in the volatile products after freeze-drying.

B. MOISTURE CONTENT DETERMINATION

The moisture content was determined as the percent of weight loss at 110° on dynamic thermogravimetric analysis (TG) of the sample, described in paragraph H.

C. ETHER EXTRACTION

The foliage samples were extracted with reagent grade ether in a Soxhlet extraction apparatus. About 2 g of the sample were weighed into an extraction thimble and placed in the extractor. The solvent (about 125 ml) was placed in a 250 ml distillation flask, and extraction was carried out for 48 hours at a rate of at least 6 cycles per hour. The extraction thimble was then removed from the extractor, dried in a vacuum dessicator

at 40° for 24 hours and weighed to determine the amount of extractives. The percent of extractives is based on the dry weight of the sample before extraction.

D. BENZENE-ETHANOL EXTRACTION

Part of the ether extracted samples were further extracted with 2:1 (v/v) benzene-ethanol solution by the method described for the ether extraction. The percent of benzene-ethanol extractives is based on the dry weight of the sample before ether extraction, i.e., the dry weight of the original sample.

E. ELEMENTAL ANALYSIS

The carbon and hydrogen contents of the unextracted, ether extracted and benzene-ethanol extracted samples and the corresponding extractives were determined by Galbraith Laboratories, Inc.

F. THERMAL EVOLUTION ANALYSIS

The thermal evolution analysis (TEA) was carried out on a DuPont Model 916 Thermal Evolution Analyzer. The samples for analysis were weighed to the nearest microgram using a Cahn R-100 electrobalance equipped with a digital voltmeter. A 700-800 μg sample was heated under flowing nitrogen (30 ml/min) from room temperature to 500° at a linear rate of 16 degrees per minute. The detector response was recorded simultaneously as a function of temperature on a DuPont Model 990 Thermal Analyzer, and as a function of time on a recorder equipped with a disc integrator. The integration was calculated up to 500° to determine the total carbon evolution. Inositol was selected from the screening experiments as a suitable calibration standard. To minimize errors due to gas flow variations, the

flows were checked frequently and an inositol standard was run twice daily.

The percent of carbon evolved from a foliage sample as combustible volatiles was calculated from TEA data and elemental analysis data as illustrated in the following formula:

$$\% \text{ of carbon evolved as combustible volatiles} = \frac{\mu g \text{ of C evolved}}{\text{wt. of sample} \times \% \text{ C of sample}}$$

The distribution of combustible volatiles over different temperature ranges can be evaluated from the ratio of the integrator counts within each range to the total counts at 500°. For better comparison between sample treatments, the TEA data for extracted samples were also calculated on the basis of the original unextracted sample weight from the extractive content and carbon content of the extracted sample, and these modified values were divided into 50° temperature intervals.

The previous study revealed a linear correlation between the heat of combustion and the carbon content of the natural fuel samples.[2] If we consider the percent combustible carbon value in a given temperature range as the "percent of carbon content" of the combustible gas, the TEA data can be converted to heat of combustion of the volatiles using the following formula:

$$\Delta H_{comb.}^{400^\circ} \text{ (cal/g)} = \% \text{ Carbon} \times 94.45 - 163.8$$

According to the above formula, for small evolved carbon values (less than 1.7%), as in the initial stages of decomposition, the heat value is negative. Since this negative heat of combustion is impossible, these

values are given in parentheses and considered zero for the cumulative results. However, the difference in calculated values was used to determine the heat evolved in temperature intervals.

G. HEATING AND GAS CHROMATOGRAPHY

The foliage samples were also subjected to heating and subsequent GLC of the volatiles. About 3 mg of the unextracted, ether extracted and benzene-ethanol extracted samples were heated in a micro-furnace which was connected directly to the GLC injection port. This micro-furnace can be heated to 250° in less than 10 seconds and then rapidly cooled to room temperature. In this way the changes in volatile components evolved at low temperatures after each treatment were determined without the complications caused by pyrolytic reactions due to prolonged heating. The volatiles were carried through a 12' x 1/8" 5% carbowax column by nitrogen (25 ml/min). The column was heated from 50° to 200° at a programmed rate of 10°/min and the volatile compounds detected by flame ionization.

The concentrated ether and benzene-ethanol extractive solutions were injected directly and analyzed by GLC under the same conditions. The volatile components evolved from heating the foliage samples can thus be identified as ether extractable materials or benzene-ethanol extractable materials. No attempt has been made to identify or quantify the individual volatile components in this study.

H. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TG) was carried out on a Cahn R-100 electrobalance equipped with a furnace tube which was programmed at 15°/min

by the DuPont Model 990 Thermal Analyzer. Two milligram samples were heated from room temperature to 500° under nitrogen flow (75 ml/min). The derivatives of the TG curve, DTG, was provided simultaneously by a Cahn Time Derivative Computer.

III. DISCUSSION OF RESULTS

The results in Table 1 show that the extractive content of foliage varies widely with species, and that most samples contain two to three times more benzene-ethanol extractives than ether extractives. Exceptions are aspen, where the two fractions are nearly equal and sawtooth palmetto where the benzene-ethanol fraction is nearly six times as large.

The elemental analysis results given in Tables 2 and 3 show that, in general, the foliage and benzene-ethanol extractives are of similar composition, but the ether extractives have a much higher carbon content. This is an expected result, because ether extraction removes the less polar components from foliage tissues. The average carbon content of ether extractives is about 70%, compared to about 48% for the benzene-ethanol extractives or about 6450 cal/g compared to 4370 for benzene-ethanol extractives, indicating that ether extractives contribute about 50% more heat on a weight basis.

The combustible carbon and heat release data given in Tables 14-22, are displayed graphically in Figs. 1-9 for easier comparison. Part A of the figures shows the combustible carbon and heat evolved in temperature intervals, and Part B shows the cumulative combustible carbon and heat evolution . The dashed line in Part B shows the position of the zero heat value calculated from the heat equivalance equation. These

graphs show a direct relationship between extractive content and heat release and the importance of the contribution of the extractives to the heat release. For example, more than 60% of the effective heat content of aspen foliage is contributed by the extractives. This suggests that seasonal changes in the extractive content could result in profound changes in the flammability of natural fuels.

These results also show that differences exist among the three treatments throughout the whole heating period. This indicates both the ether extractives and the benzene-ethanol extractives contain high boiling-point materials which are retained by the foliage tissues and evolve or, most likely, pyrolyze at high temperatures.

The heat release as a function of temperature from the original foliage samples, as shown in part A is generally of two basic patterns. In the first pattern, the evolution of combustible volatiles and heat increases with temperature until it reaches 300-400°, then sharply decreases and forms a bias bell shape pattern. All the coniferous species, as well as aspen and sawtooth palmetto, give this pattern. In the second pattern, the evolution of combustible volatiles and heat reaches its maximum rate at 250-300°, then levels off to form a plateau until 450°. In some cases, it forms double peaks on the plateau. Chamise, gallberry, and manzanita give the second pattern. The formation of the second pattern is mainly caused by the high concentration of combustible carbon evolved from ether and benzene-ethanol extractives between 250-300° and also from 350-450°.

Examination of the differences between the heat release profiles among the three treatments, shows the differences between the original samples and the ether extracted samples are, in most cases, evenly distributed from

200-450°. For chamise, gallberry and manzanita, however, the differences between 250-450° (250-400° for manzanita) are much larger than the differences between 200-250°. This suggests the ether extractives of these three species contain materials which vaporize or pyrolyze mainly between 250-450°. The TG (thermogravimetry) of the ether extractives of manzanita, a representative of these three species, shown in Fig. 19 confirms this assumption. The TG of the ether extractives of ponderosa pine, a representative of the first group, shown in Fig. 20, shows a more consistent weight loss from low temperatures to 450°.

The differences between the ether extracted and benzene-ethanol extracted samples are always larger below 300°. This suggests that benzene-ethanol extractives vaporize or alternatively, pyrolyze and char before 300°. The TG's of benzene-ethanol extractives of manzanita and ponderosa pine, shown in Figs. 19 and 20 confirm both of these assumptions.

Fig. 19 shows the benzene-ethanol extractives produce combustible volatiles earlier than the ether extractives of manzanita. This is a surprising result because it is expected that benzene-ethanol extractives are more polar and hence, less volatile than ether extractives. However, the volatility also depends on the molecular weight, which must be dominant in this case.

As indicated before, the benzene-ethanol extractive content of foliage is two to three times higher than the ether extractive content. However, the accumulated combustible carbon and heat evolution curves shown in part B of Figs. 1-9 show that the differences between the unextracted and ether extracted samples are, in most cases, much larger than the differences between the ether extracted and benzene-ethanol extracted samples. This indicates that the ether extractives contribute more heat than the benzene-

ethanol extractives, although they are less abundant in the plant tissues. The higher carbon content of ether extractives and the higher yield of char from benzene-ethanol extractives account for this result.

As shown in the cumulative heat evolution curves, none of the samples evolves a meaningful amount of heat before 200°, but by 300° all the unextracted fuels evolve more than 500 cal/g, well above the heat of preignition of forest fuels, which range from 200-300 cal/g.[3,6] Therefore, the minimum ignition temperature of all foliage fuels is between 200 and 300°.

It seems more meaningful to judge the ignitibility of these fuels by the heat release as a function of temperature. The evolution of a large amount of combustible carbon and heat in a narrow temperature range at lower temperatures should indicate high ignitibility in a fuel. Based on this standard, the samples which give the second diagram pattern, i.e., chamise, gallberry and manzanita, should be highly ignitible, because they release high concentrations of combustible carbon between 250-300°.

The results of this study seem to suggest that benzene-ethanol extractives are more important in the ignition of foliage because they tend to release combustible volatiles before 300°. They are especially important for the ignition of chamise, gallberry and manzanita, because in these species the ether extractives release combustible volatiles only at higher temperatures (above 250°). Ether extractives, however, are more important in sustaining the flaming combustion at high temperatures.

The heating and GLC analysis results shown in Figs. 10-18 indicate the volatile compounds released on heating foliage samples were not all removed by extraction. Some of the peaks were removed by ether extraction, some

by benzene-ethanol extraction and some still remain in the tissue after the two step extractions. In some extreme cases, such as in chamise and manzanita, all the original GLC peaks were still present after two step extractions. Conversely, the major components removed by extraction are not necessarily volatilized by heating. For example, the large peak having a retention time of 9 minutes on the chromatogram of the ether extractives of Douglas fir (Fig. 12-B), and the major peak at 12.5 minutes on the chromatogram of the ether extractives of slash pine (Fig. 18-B) are both absent in the chromatograms of the volatiles of the original fuels (Figs. 12-A and 18-A). The extraction method, therefore, is not specific for the heat release at low temperatures, although it does give valuable information about the relative roles which the ether-extractives and benzene-ethanol extractives play in the ignition and combustion of foliage fuels.

IV. FUTURE PLANS

Thermal evolution analysis has been established as a convenient method for determining the temperature dependence of heat release in forest fuels. The study can now be extended to determine the variations in heat release profiles and heat of combustion resulting from natural changes in the chemical composition of forest fuels, particularly during the fire season.

The GLC analysis in this study suggests that chemical extraction is not the best approach to evaluation of the heat content available at low temperatures. In future studies, the volatile compounds will be removed specifically by heating. Bomb calorimeter runs before and after this heat extraction will establish the actual heat value of the volatiles and

provide a standard for further evaluation of the TEA method. Identification of the compounds removed by heat extraction will provide a basis for their quantitative determination.

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Table 1. Moisture, Ether Extractives, Benzene-Ethanol Extractives and Total Extractives Content of Foliage Samples.[a]

Sample	M.C. (%)	Ether Extractives (%)	Benzene-Ethanol Extractives (%)	Total Extractives (%)
Aspen	1.9	16.8	19.8	36.6
Chamise	1.9	7.6	15.0	22.6
Douglas Fir	2.0	11.2	19.1	30.3
Gallberry	2.2	11.8	32.8	44.6
Lodgepole Pine	2.1	6.4	19.6	26.0
Manzanita	1.8	9.5	16.3	25.8
Ponderosa Pine	2.3	11.8	19.0	30.8
Sawtooth Palmetto	1.7	1.9	11.2	13.1
Slash Pine	1.7	9.1	18.0	27.1

[a]All the figures are based on dry, unextracted sample weight.

Table 2. Carbon and Hydrogen Content of Foliage Samples.[a]

Sample	Unextracted (%)		Ether Extracted (%)		Benzene-Ethanol Extracted (%)	
	C	H	C	H	C	H
Aspen	49.78	6.16	45.80	6.37	44.31	5.80
Chamise	51.97	6.84	48.33	6.54	48.94	6.64
Douglas Fir	52.87	7.78	48.57	6.34	48.34	5.99
Gallberry	54.44	6.37	50.32	6.45	49.41	6.67
Lodgepole Pine	52.06	6.47	49.15	6.38	47.64	6.09
Manzanita	51.82	6.52	48.48	6.24	49.42	6.42
Ponderosa Pine	48.62	5.84	47.95	6.48	47.81	6.44
Sawtooth Palmetto	50.38	5.25	48.08	6.20	48.28	5.84
Slash Pine	51.31	6.49	45.36	5.92	47.88	5.92

[a]All figures are based on dry sample weight.

Table 3. Carbon and Hydrogen Content of Ether and Benzene-Ethanol Extractives of Foliage Samples.

Sample	Ether Extractives (%)		Benzene-Ethanol Extractives (%)	
	C	H	C	H
Aspen	73.28	11.77	47.42	6.75
Chamise	72.16	10.30	45.09	6.92
Douglas Fir	59.84	9.03	55.94	8.13
Gallberry	76.53	11.36	50.78	6.45
Lodgepole Pine	68.26	9.78	48.62	7.45
Manzanita	76.84	10.89	46.22	6.46
Ponderosa Pine	61.29	8.64	47.07	7.34
Sawtooth Palmetto	70.42	10.40	--	--
Slash Pine	--	--	44.39	7.26

Table 4. Percent of Carbon Evolved as Combustible Volatiles from Foliage Samples Heated to 500°[a]

Sample	Unextracted (%)	Ether Extracted (%)	Benzene-Ethanol Extracted (%)
Aspen	76.3	60.5	56.3
Chamise	72.7	56.6	54.5
Douglas Fir	69.0	61.7	61.0
Gallberry	75.8	64.7	67.5
Lodgepole Pine	60.8	61.7	58.5
Manzanita	70.0	54.2	51.2
Ponderosa Pine	66.6	58.1	52.5
Sawtooth Palmetto	56.0	53.5	58.6
Slash Pine	71.3	61.7	57.3

[a] All figures are based on the weight of carbon in the sample.

Table 5. Temperature Distribution of Combustible Carbon Evolved from Aspen Foliage

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracted	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	0.5	0.5
150-200	1.4	1.4	0.8	0.8	1.6	2.1
200-250	12.4	13.8	13.1	13.9	6.2	8.3
250-300	20.8	34.6	18.5	32.4	15.1	23.4
300-350	28.2	62.8	28.3	60.7	31.5	54.9
350-400	17.9	80.7	17.8	78.5	22.2	77.1
400-450	12.5	93.2	13.6	92.1	13.5	90.6
450-500	6.8	100.0	7.9	100.0	9.4	100.0

Table 6. Temperature Distribution of Combustible Carbon Evolved from Chamise Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracte	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	0.9	0.9
150-200	0.8	0.8	0.9	0.9	3.1	4.0
200-250	7.0	7.8	8.3	9.2	5.2	9.2
250-300	21.2	29.0	20.7	29.9	13.9	23.1
300-350	21.3	50.3	19.2	49.1	21.3	44.4
350-400	21.0	71.3	20.9	70.0	23.1	67.5
400-450	19.5	90.8	19.6	89.6	21.9	89.4
450-500	9.2	100.0	10.4	100.0	10.6	100.0

Table 7. Temperature Distribution of Combustible Carbon Evolved from Douglas Fir Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracted	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0.4	0.4	0	0	0	0
100-150	0.5	0.9	0	0	0	0
150-200	2.1	3.0	1.3	1.3	1.3	1.3
200-250	10.7	13.7	9.4	10.7	4.3	5.6
250-300	14.2	27.9	13.9	24.6	9.3	14.9
300-350	21.3	49.2	22.1	46.7	24.1	39.0
350-400	29.0	78.2	30.6	77.3	34.8	73.8
400-450	16.4	94.6	15.9	93.2	18.2	92.0
450-500	5.4	100.0	6.8	100.0	8.0	100.0

Table 8. Temperature Distribution of Combustible Carbon from Gallberry Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracte	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	0.6	0.6
150-200	0.7	0.7	1.1	1.1	1.9	2.5
200-250	8.9	9.6	11.6	12.7	6.1	8.6
250-300	23.8	33.4	24.9	37.6	17.5	26.1
300-350	19.0	52.4	19.1	56.7	24.6	50.7
350-400	19.4	71.8	18.1	74.8	19.3	70.0
400-450	21.1	92.9	17.9	92.7	20.0	90.9
450-500	7.1	100.0	7.3	100.0	10.0	100.0

Table 9. Temperature Distribution of Combustible Carbon Evolved from Lodgepole Pine Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracte	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	0	0
150-200	1.0	1.0	1.3	1.3	1.0	1.0
200-250	7.5	8.5	7.0	8.3	3.3	4.3
250-300	14.8	23.3	16.5	24.8	10.4	14.7
300-350	23.5	46.8	24.0	48.8	27.9	42.6
350-400	29.5	76.3	28.3	77.1	32.6	75.2
400-450	16.8	93.1	16.1	93.2	17.1	92.3
450-500	6.9	100.0	6.8	100.0	7.7	100.0

Table 10. Temperature Distribution of Combustible Carbon Evolved from Manzanita Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracted	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	1.6	1.6
150-200	1.3	1.3	0.7	0.7	2.9	4.5
200-250	9.1	10.4	12.6	13.3	6.0	10.5
250-300	27.0	37.4	20.8	34.1	15.1	25.6
300-350	19.0	56.4	15.7	49.8	16.8	42.4
350-400	20.9	77.3	18.8	68.6	20.1	62.5
400-450	16.6	93.9	22.7	91.3	26.4	88.9
450-500	6.1	100.0	8.7	100.0	11.1	100.0

Table 11. Temperature Distribution of Combustible Carbon Evolved from Ponderosa Pine Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracte	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	0	0
150-200	3.3	3.3	1.2	1.2	0.8	0.8
200-250	11.2	14.5	9.0	10.2	3.6	4.4
250-300	15.2	29.7	16.7	26.9	14.6	19.0
300-350	25.8	55.5	25.6	52.5	34.9	53.9
350-400	23.5	79.0	25.5	78.0	25.7	79.6
400-450	14.6	93.6	15.3	93.3	13.0	92.6
450-500	6.4	100.0	6.7	100.0	7.4	100.0

Table 12. Temperature Distribution of Combustible Carbon Evolved from Sawtooth Palmetto Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracted	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0	0	0	0	0.9	0.9
150-200	0	0	0.9	0.9	3.4	4.3
200-250	3.7	3.7	3.4	4.3	5.1	9.4
250-300	20.7	24.4	20.0	24.3	19.3	28.7
300-350	34.6	59.0	32.7	57.0	33.1	61.8
350-400	24.9	83.9	27.5	84.5	26.1	87.9
400-450	10.9	94.8	9.5	94.0	8.2	96.1
450-500	5.2	100.0	6.0	100.0	3.9	100.0

Table 13. Temperature Distribution of Combustible Carbon Evolved from Slash Pine Foliage.

Temp. (°C)	Unextracted		Ether Extracted		Benzene-Ethanol Extracted	
	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)	Evolved C (%)	Cumulative (%)
50-100	0	0	0	0	0	0
100-150	0.4	0.4	0	0	0.3	0.3
150-200	2.3	2.7	1.1	1.1	2.1	2.4
200-250	10.1	12.8	6.5	7.6	5.8	8.2
250-300	16.3	29.1	14.6	22.2	13.6	21.8
300-350	24.5	53.6	26.6	48.8	27.2	49.0
350-400	29.3	82.9	32.1	80.9	32.2	81.2
400-450	12.7	95.6	13.6	94.5	12.2	93.4
450-500	4.4	100.0	5.5	100.0	6.6	100.0

Table 14. The Evolution of Combustible Carbon and Heat from Aspen Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)[b]	0	0(-160)	0	0(-160)
100-150	0	0	0	0	0.1	0.1	0	0(-160)	0	0(-160)	10	0(-150)
150-200	0.5	0.5	0.2	0.2	0.2	0.3	40	0(-120)	20	0(-140)	10	0(-140)
200-250	4.7	5.2	3.0	3.2	1.0	1.3	450	330	280	140	100	0(-40)
250-300	7.9	13.1	4.3	7.5	2.4	3.7	740	1070	400	540	230	190
300-350	10.8	23.9	6.5	14.0	5.0	8.7	1020	2090	620	1160	470	660
350-400	6.7	30.6	4.1	18.1	3.5	12.2	640	2730	390	1550	330	990
400-450	4.8	35.4	3.2	21.3	2.1	14.3	450	3180	300	1850	200	1190
450-500	2.6	38.0	1.8	23.1	1.5	15.8	250	3430	170	2020	140	1330

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 15. The Evolution of Combustible Carbon and Heat from Chamise Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)[b]	0	0(-160)	0	0(-160
100-150	0	0	0	0	0.2	0.2	0	0(-160)	0	0(-160)	20	0(-140
150-200	0.3	0.3	0.2	0.2	0.6	0.8	20	0(-140)	20	0(-140)	50	0(-90)
200-250	2.6	2.9	2.1	2.3	1.1	1.9	250	110	190	50	110	20
250-300	8.1	11.0	5.3	7.6	2.9	4.8	770	880	500	550	270	290
300-350	8.0	19.0	4.8	12.4	4.3	9.1	750	1630	460	1010	410	700
350-400	8.0	27.0	5.3	17.7	4.8	13.9	760	2390	500	1510	450	1157
400-450	7.3	34.3	5.0	22.7	4.5	18.4	690	3080	470	1980	420	1570
450-500	3.5	37.8	2.6	25.3	2.2	20.6	330	3410	250	2230	210	1780

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 16. The Evolution of Combustible Carbon and Heat from Douglas Fir Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0.1	0.1	0	0	0	0	10	0(-150)[b]	0	0(-160)	0	0(-160)
100-150	0.2	0.3	0	0	0	0	10	0(-140)	0	0(-160)	0	0(-160)
150-200	0.8	1.1	0.3	0.3	0.3	0.3	80	0(-60)	20	0(-140)	20	0(-140)
200-250	3.9	5.0	2.5	2.8	0.9	1.2	360	300	240	100	90	0(-50)
250-300	5.2	10.2	3.7	6.5	1.9	3.1	500	800	350	450	180	130
300-350	7.8	18.0	5.9	12.4	4.9	8.0	740	1540	560	1010	460	590
350-400	10.5	28.5	8.2	20.6	7.2	15.2	990	2530	770	1780	680	1270
400-450	6.0	34.5	4.2	24.8	3.8	19.0	560	3090	400	2180	360	1630
450-500	2.0	36.5	1.8	26.6	1.6	20.6	190	3280	170	2350	150	1780

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 17. The Evolution of Combustible Carbon and Heat from Gallberry Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)[a]	0	0(-160)	0	0(-160)
100-150	0	0	0	0	0.1	0.1	0	0(-160)	0	0(-160)	10	0(-150)
150-200	0.3	0.3	0.3	0.3	0.4	0.5	20	0(-140)	20	0(-140)	30	0(-120)
200-250	3.7	4.0	3.3	3.6	1.1	1.6	350	210	320	180	110	0(-10)
250-300	9.8	13.8	7.2	10.8	3.2	4.8	930	1140	680	860	300	290
300-350	7.8	21.6	5.5	16.3	4.6	9.4	740	1880	520	1380	430	720
350-400	8.1	29.7	5.2	21.5	3.6	13.0	760	2640	490	1870	340	1060
400-450	8.7	38.4	5.1	26.6	3.7	16.7	820	3460	480	2350	350	1410
450-500	2.9	41.3	2.1	28.7	1.8	18.5	280	3740	200	2550	170	1580

[a]Calculated by difference from cumulative values.

[b]Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 18. The Evolution of Combustible Carbon and Heat from Lodgepole Pine Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	o	0	0	0	0(-160)[b]	0	0(-160)	0	0(-160)
100-150	0	0	0	0	0	0	0	0(-160)	0	0(-160)	0	0(-160)
150-200	0.3	0.3	0.4	0.4	0.2	0.2	20	0(-140)	30	0(-130)	20	0(-140)
200-250	2.4	2.7	2.0	2.4	0.7	0.9	230	90	190	60	60	0(-80)
250-300	4.7	7.4	4.6	7.0	2.1	3.0	450	540	440	500	200	120
300-350	7.4	14.8	6.9	13.9	5.8	8.8	690	1230	650	1150	550	670
350-400	9.4	24.2	8.0	21.9	6.7	15.5	890	2120	750	1900	630	1300
400-450	5.3	29.5	4.6	26.5	3.5	19.0	500	2620	440	2340	330	1630
450-500	2.2	31.7	1.9	28.4	1.6	20.6	210	2830	180	2520	150	1780

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 19. The Evolution of Combustible Carbon and Heat from Manzanita Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)[b]	0	0(-160)	0	0(-160)
100-150	0	0	0	0	0.3	0.3	0	0(-160)	0	0(-160)	20	0(-140)
150-200	0.5	0.5	0.2	0.2	0.5	0.8	40	0(-120)	20	0(-140)	50	0(-90)
200-250	3.3	3.8	3.0	3.2	1.2	2.0	320	200	280	140	120	30
250-300	9.8	13.6	4.9	8.1	2.8	4.8	920	1120	460	600	260	290
300-350	6.9	20.5	3.8	11.9	3.2	8.0	650	1770	360	960	300	590
350-400	7.6	28.1	4.4	16.3	3.8	11.8	720	2490	420	1380	360	950
400-450	6.0	34.1	5.4	21.7	4.9	16.7	570	3060	510	1890	460	1410
450-500	2.2	26.3	2.1	23.8	2.1	18.8	200	3260	190	2080	190	1600

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 20. The Evolution of Combustible Carbon and Heat from Ponderosa Pine Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)[b]	0	0(-160)	0	0(-160)
100-150	0	0	0	0	0	0	0	0(-160)	0	0(-160)	0	0(-160)
150-200	1.1	1.1	0.3	0.3	0.1	0.1	100	0(-60)	20	0(-140)	10	0(-150)
200-250	3.6	4.7	2.2	2.5	0.7	0.8	340	280	210	70	60	0(-90)
250-300	4.9	9.6	4.1	6.6	2.5	3.3	460	740	390	460	240	150
300-350	8.4	18.0	6.3	12.9	6.1	9.4	800	1540	590	1050	570	720
350-400	7.6	25.6	6.3	19.2	4.5	13.9	710	2250	600	1650	430	1150
400-450	4.7	30.3	3.8	23.0	2.2	16.1	450	2700	360	2010	210	1360
450-500	2.1	32.4	1.6	24.6	1.3	17.4	200	2900	150	2160	120	1480

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 21. The Evolution of Combustible Carbon and Heat from Sawtooth Palmetto Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)[b]	0	0(-160)	0	0(-160)
100-150	0	0	0	0	0.2	0.2	0	0(-160)	0	0(-160)	20	0(-140)
150-200	0	0	0.2	0.2	0.9	1.1	0	0(-160)	20	0(-140)	80	0(-60)
200-250	1.0	1.0	0.9	1.1	1.2	2.3	90	0(-70)	80	0(-60)	110	50
250-300	5.9	6.9	5.0	6.1	4.8	7.1	560	490	470	410	460	510
300-350	9.7	16.6	8.3	14.4	8.1	15.2	910	1400	790	1200	760	1270
350-400	7.1	23.7	6.9	21.3	6.4	21.6	670	2070	650	1850	610	1880
400-450	3.0	26.7	2.4	23.7	2.0	23.6	290	2360	220	2070	190	2070
450-500	1.5	28.2	1.5	25.2	1.0	24.6	140	2500	150	2220	90	2160

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

Table 22. The Evolution of Combustible Carbon and Heat from Slash Pine Foliage as a Function of Temperature.

Temp (°C)	Percent of Original Sample Weight Evolved as Combustible Carbon						Heat Evolved (cal/g of unextracted sample)					
	Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives		Before Removal of Extractives		After Removal of Ether Extractives		After Removal of Total Extractives	
	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Percent Evolved	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative	Heat Evolved[a]	Cumulative
50-100	0	0	0	0	0	0	0	0(-160)	0	0(-160)	0	0(-160)
100-150	0.1	0.1	0	0	0.1	0.1	10	0(-150)	0	0(-160)	10	0(-150)
150-200	0.9	1.0	0.3	0.3	0.4	0.5	80	0(-70)	20	0(-140)	30	0(-120)
200-250	3.7	4.7	1.6	1.9	1.1	1.6	550	280	160	20	110	0(-10)
250-300	6.0	10.7	3.7	5.6	2.8	4.4	570	850	350	370	260	250
300-350	8.9	19.6	6.8	12.4	5.4	9.8	840	1690	640	1010	510	760
350-400	10.7	30.3	8.1	20.5	6.4	16.2	1010	2700	760	1770	610	1370
400-450	4.7	35.0	3.5	24.0	2.5	18.7	440	3140	330	2100	230	1600
450-500	1.6	36.6	1.4	25.4	1.3	20.0	150	3290	140	2240	130	1730

[a] Calculated by difference from cumulative values.

[b] Figures in parentheses are the negative calculated values which are replaced with zero in the cumulative results.

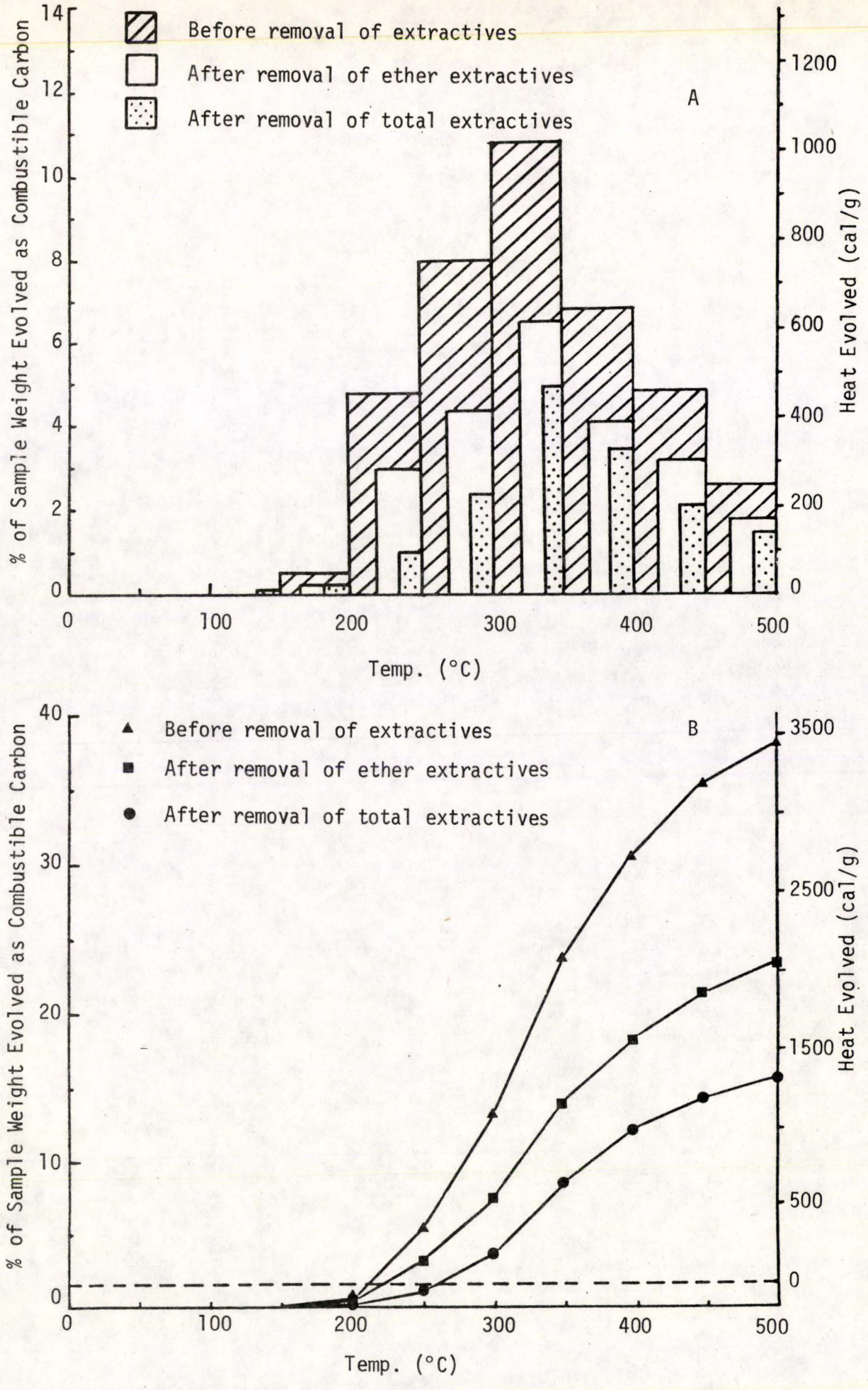
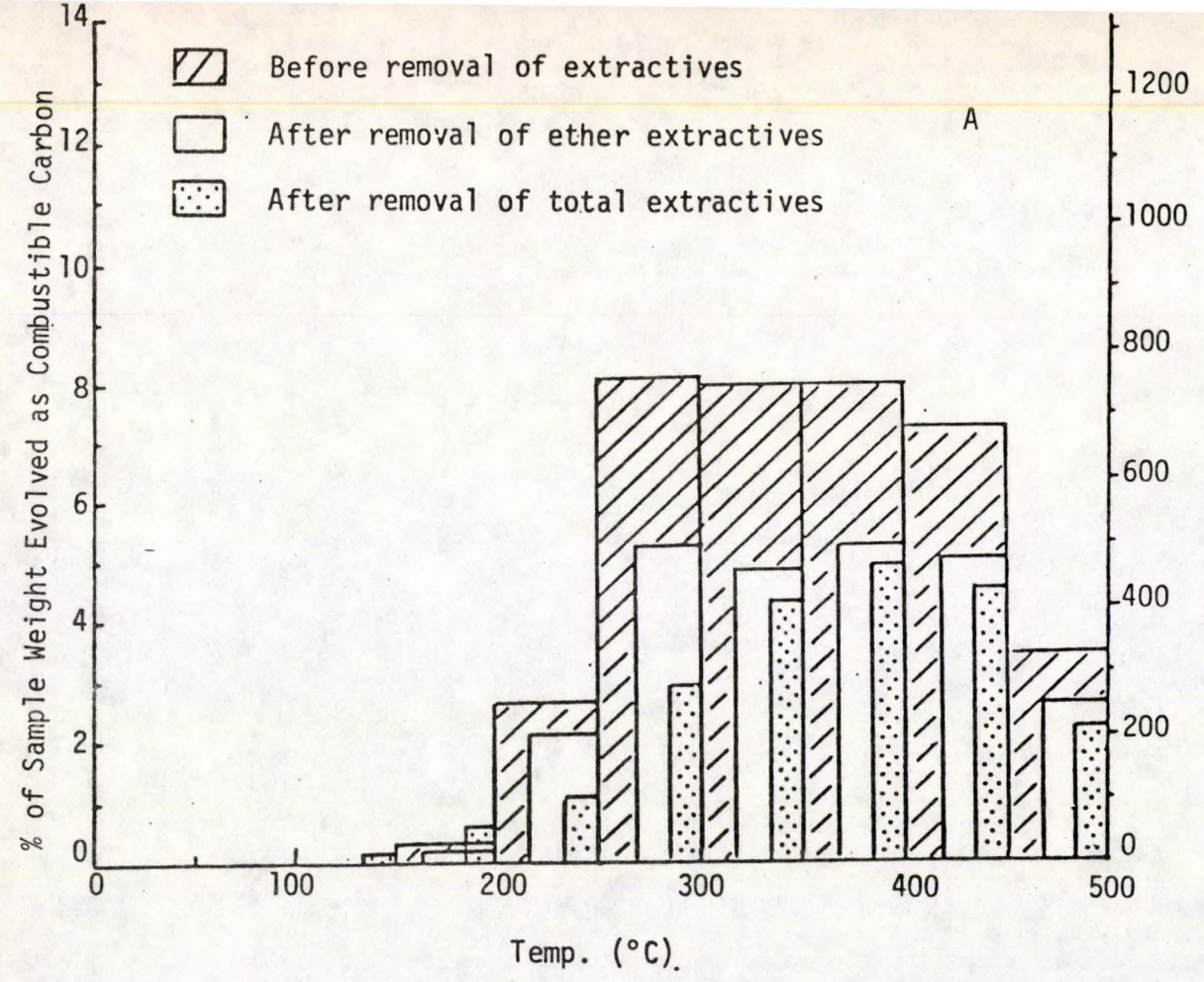


Figure 1. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from aspen foliage. (A) In temperature intervals and (B) Cumulative.



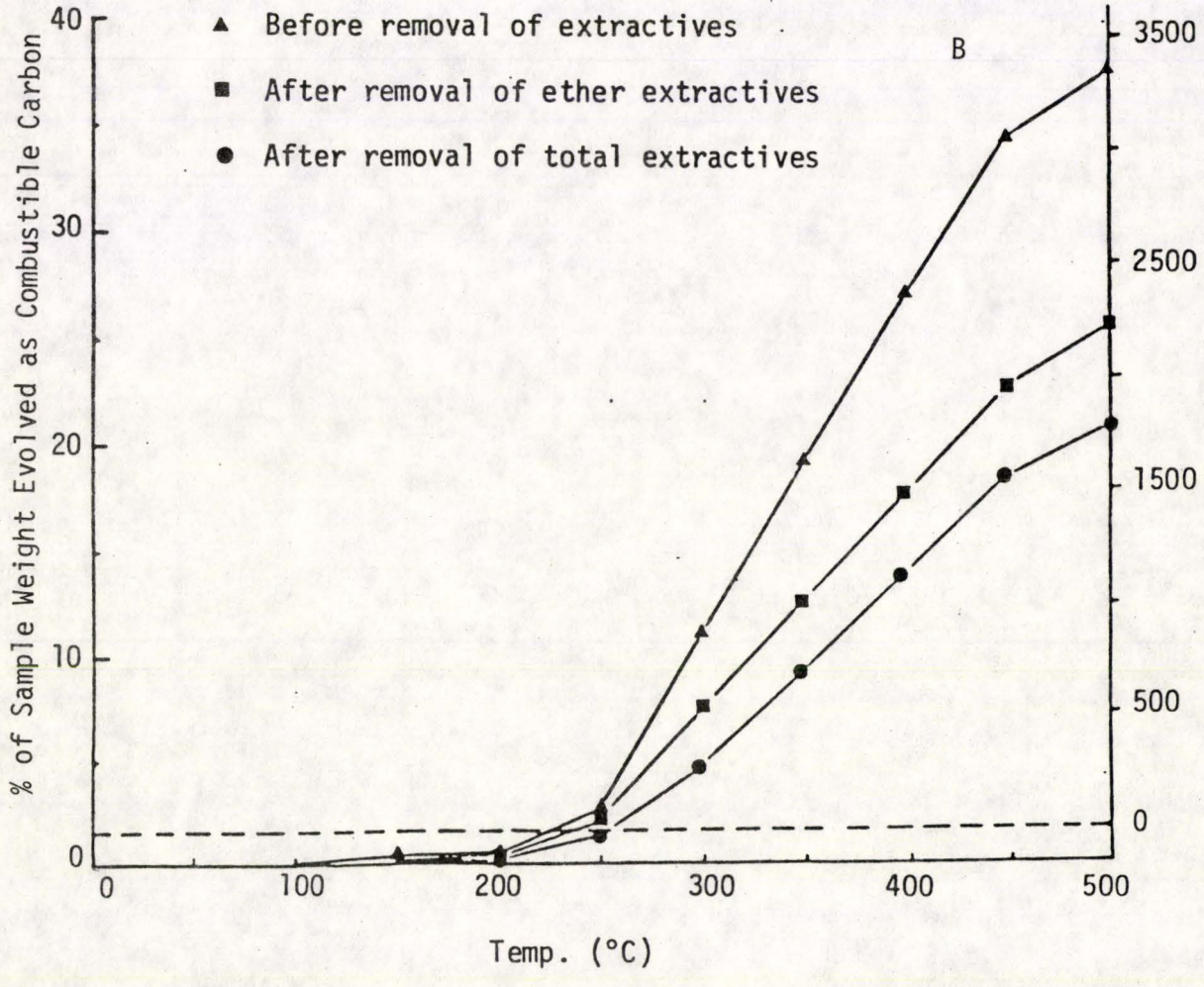
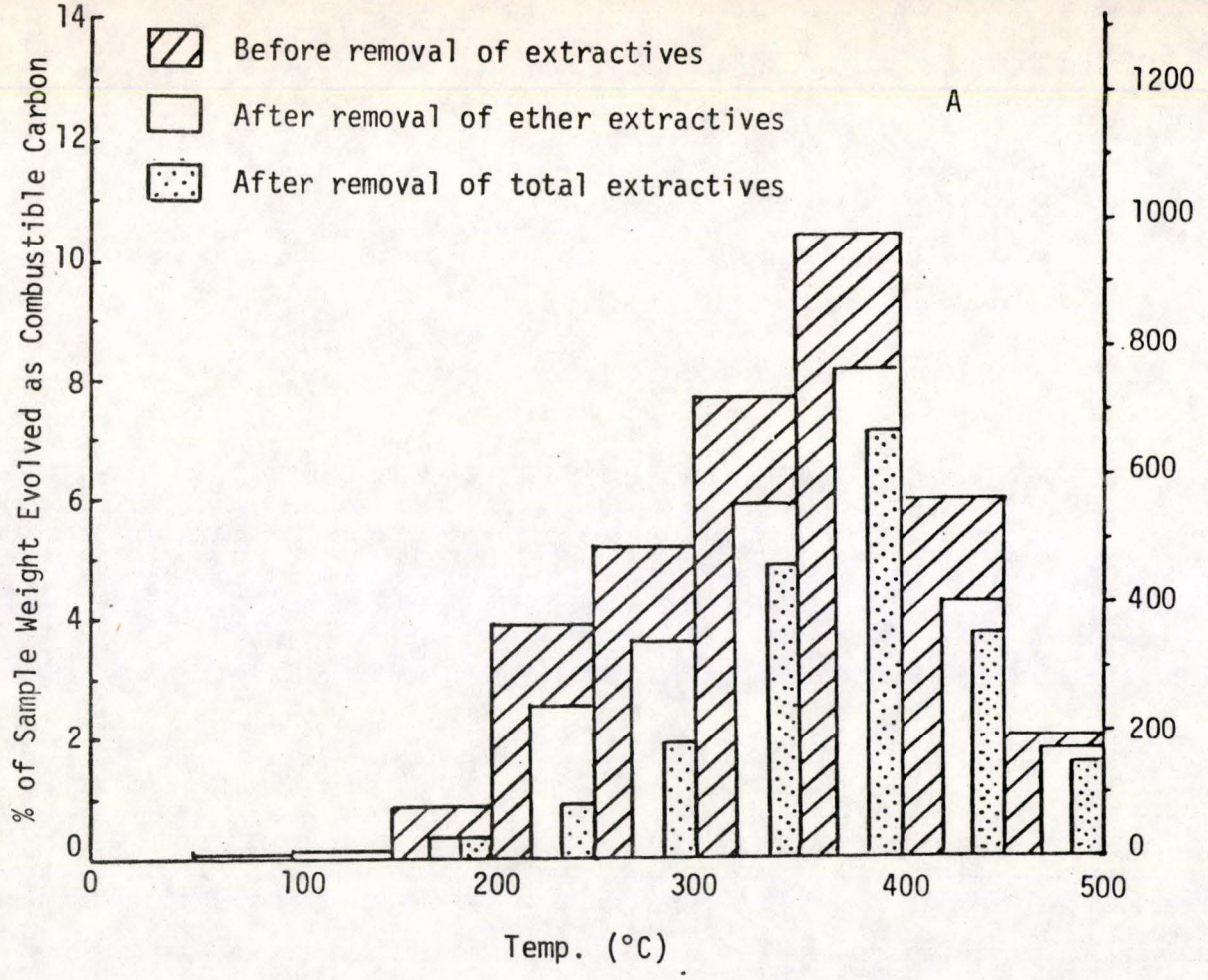


Figure 2. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from chamise foliage. (A) In temperature intervals and (B) Cumulative.



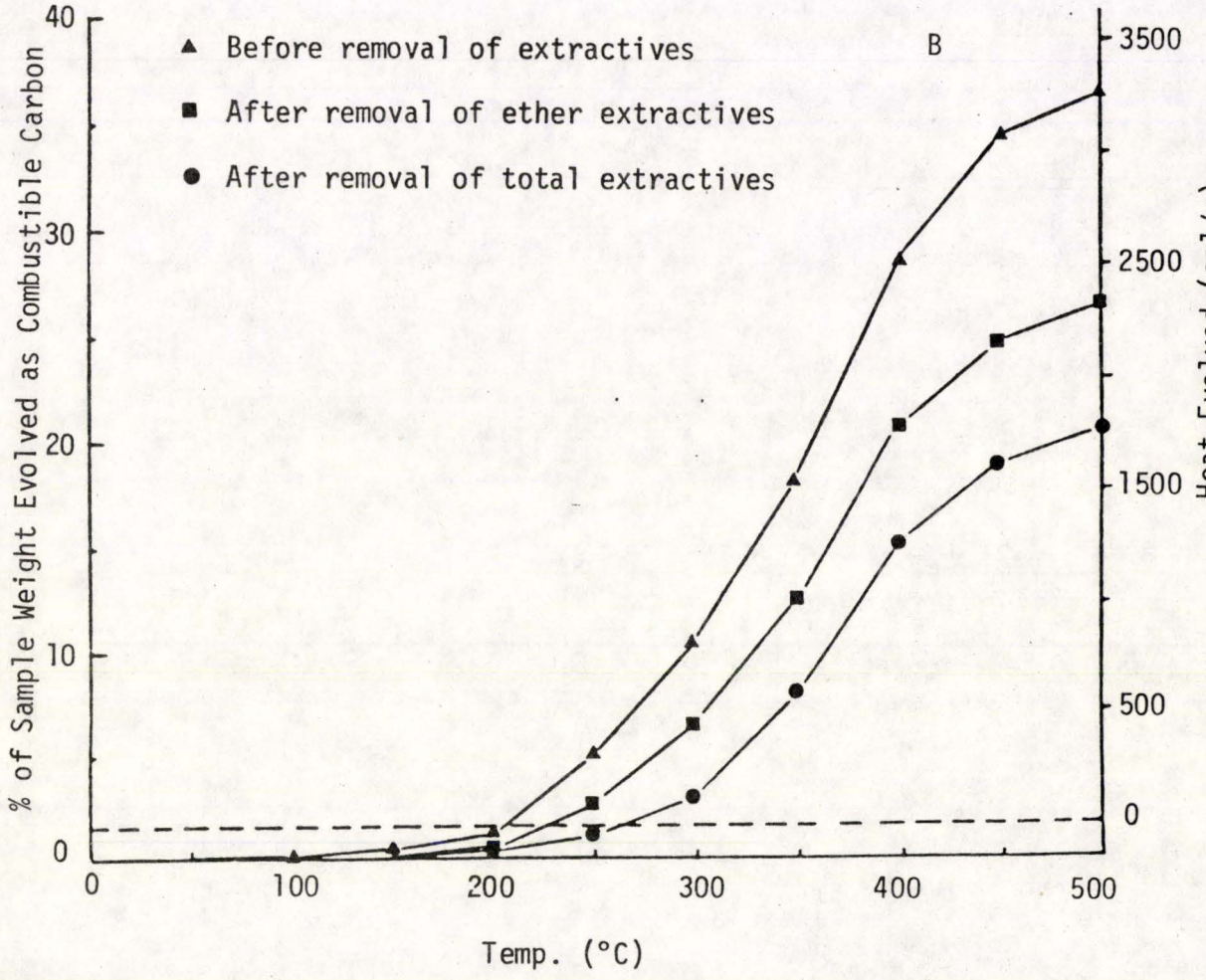


Figure 3. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from Douglas fir foliage. (A) In temperature intervals and (B) Cumulative.

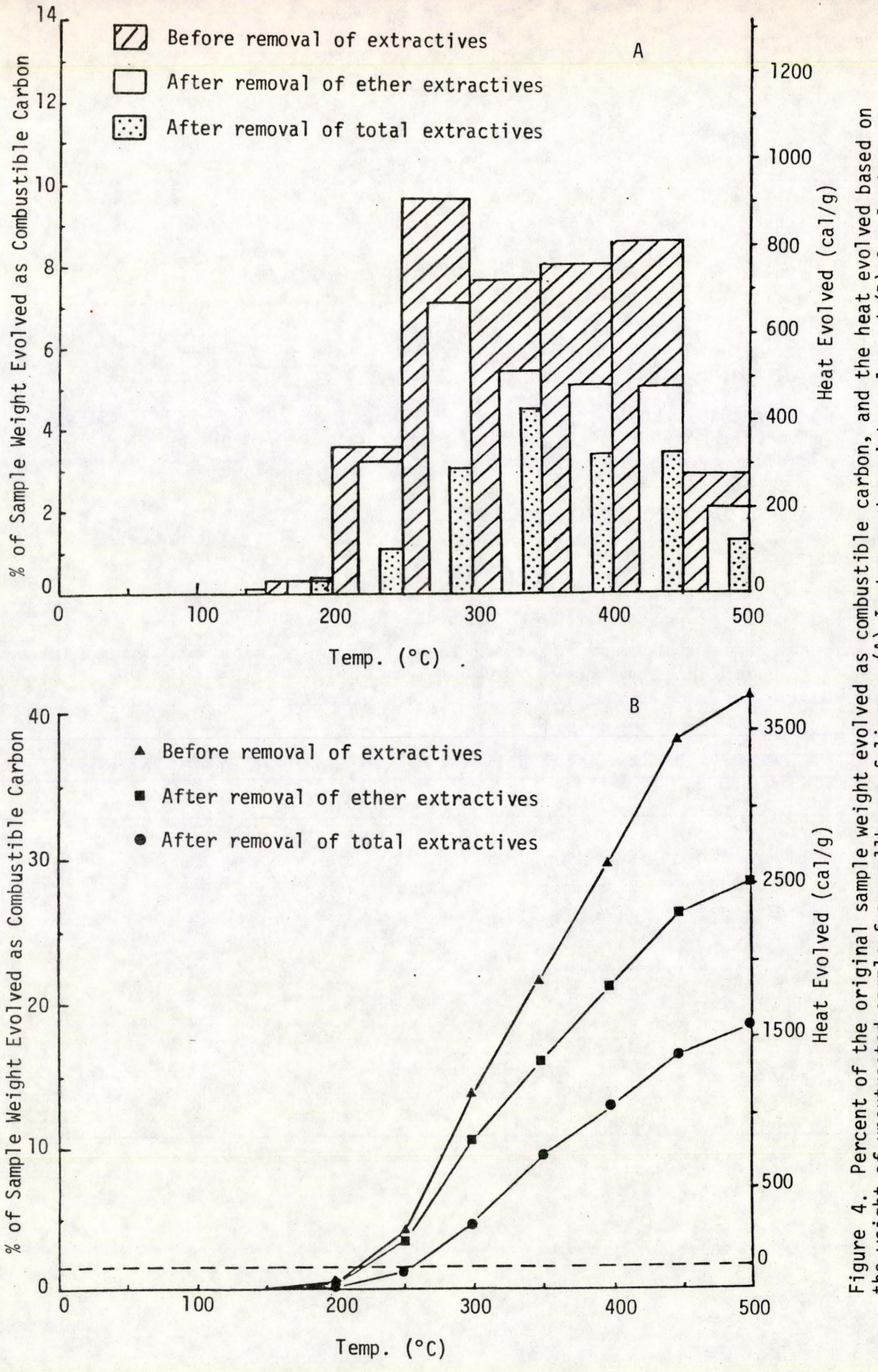
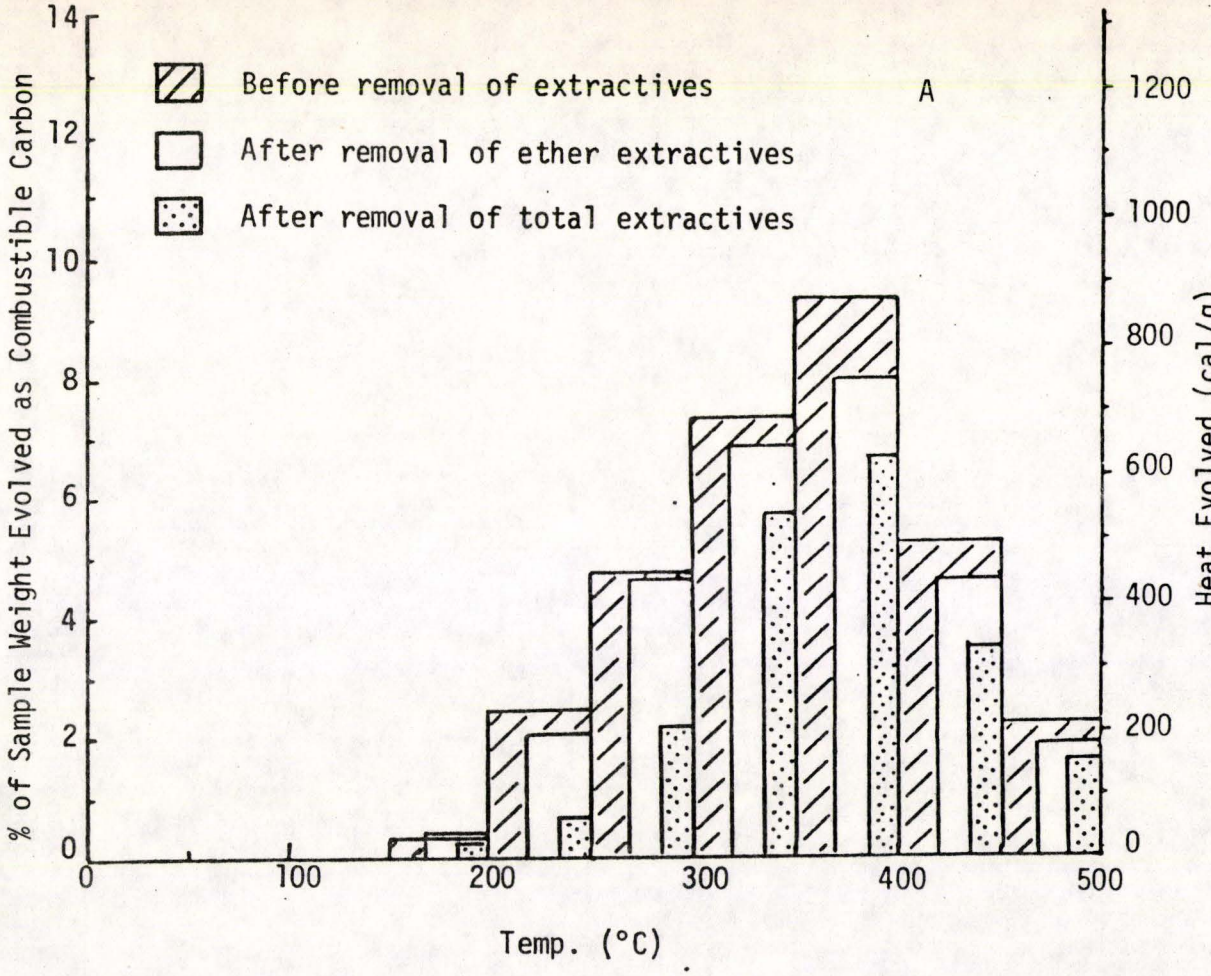

A
Before removal of extractives
After removal of ether extractives
After removal of total extractives
% of Sample Weight Evolved as Combustible Carbon
Heat Evolved (cal/g)
Temp. (°C)
B
Before removal of extractives
After removal of ether extractives
After removal of total extractives
% of Sample Weight Evolved as Combustible Carbon
Heat Evolved (cal/g)
Temp. (°C)

Figure 4. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from gallberry foliage. (A) In temperature intervals and (B) Cumulative.



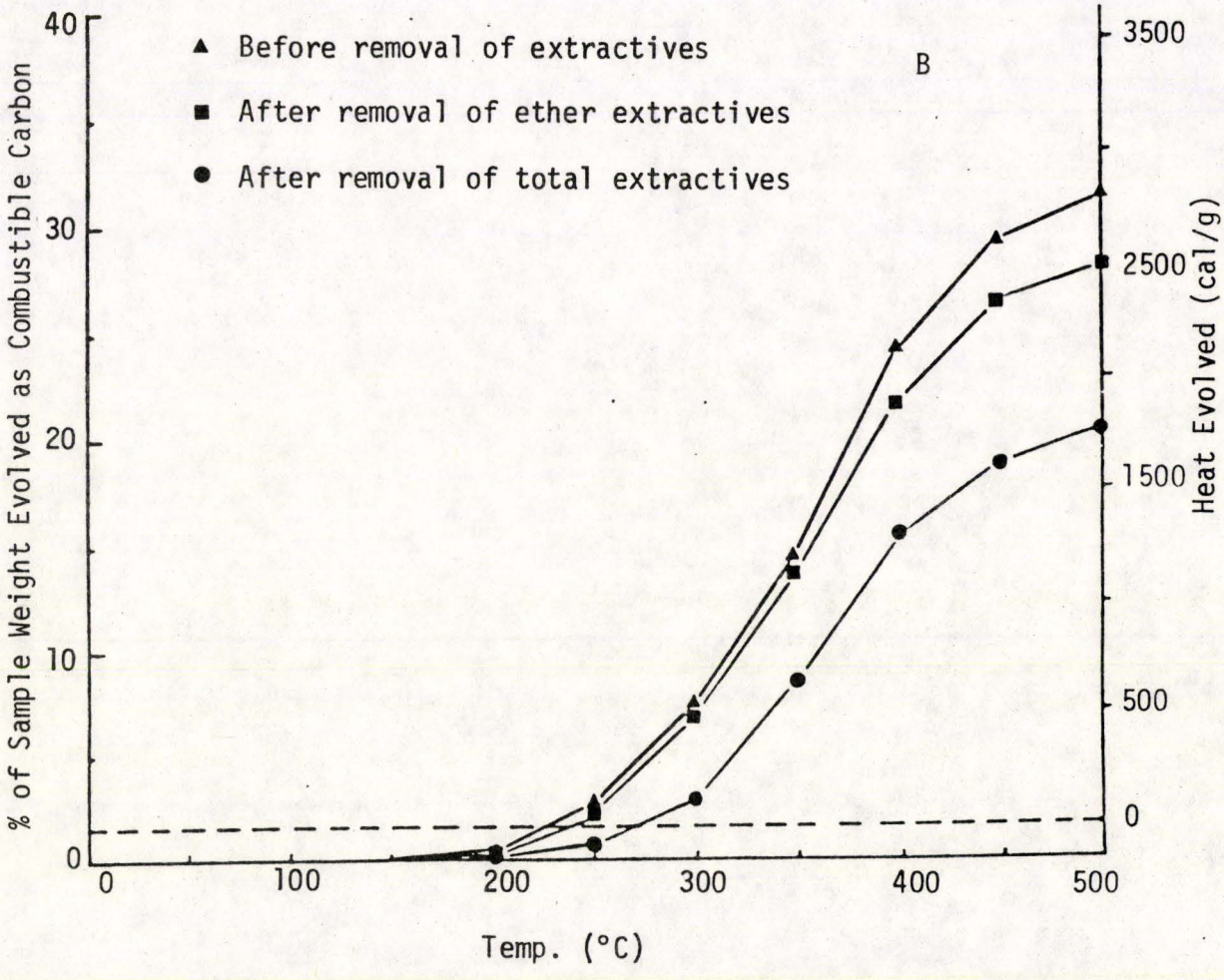
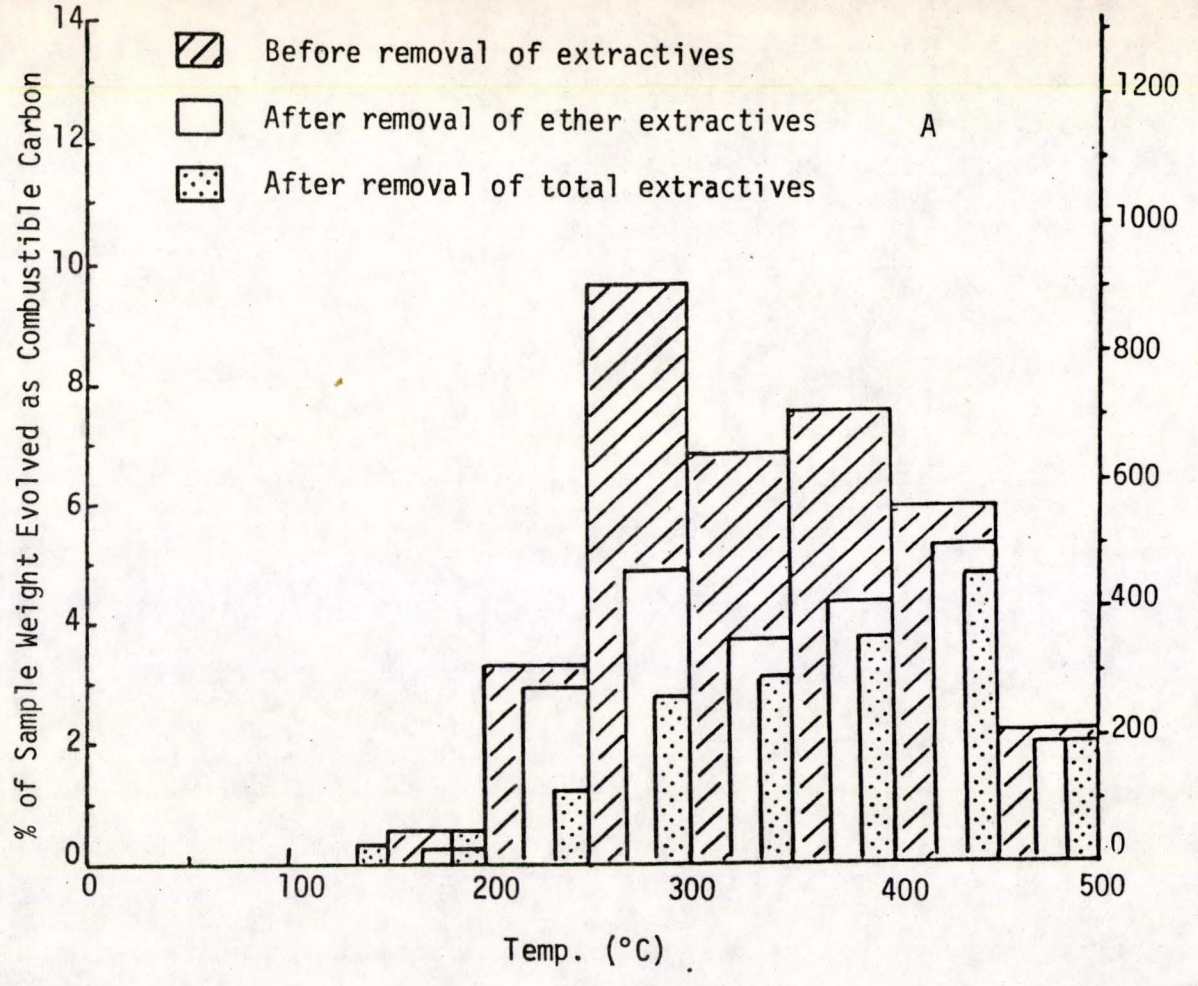


Figure 5. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from lodgepole pine foliage. (A) In temperature intervals and (B) Cumulative.



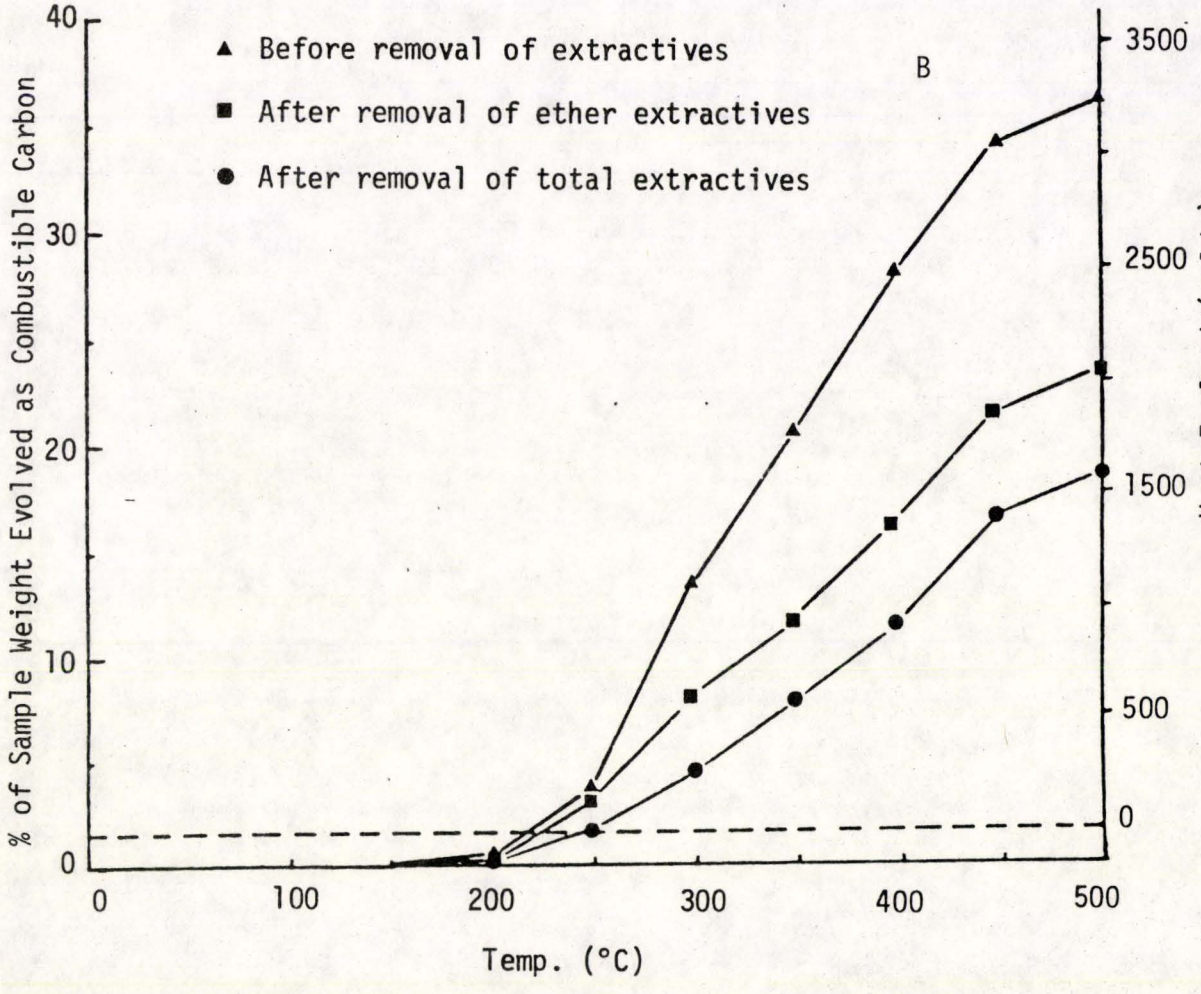
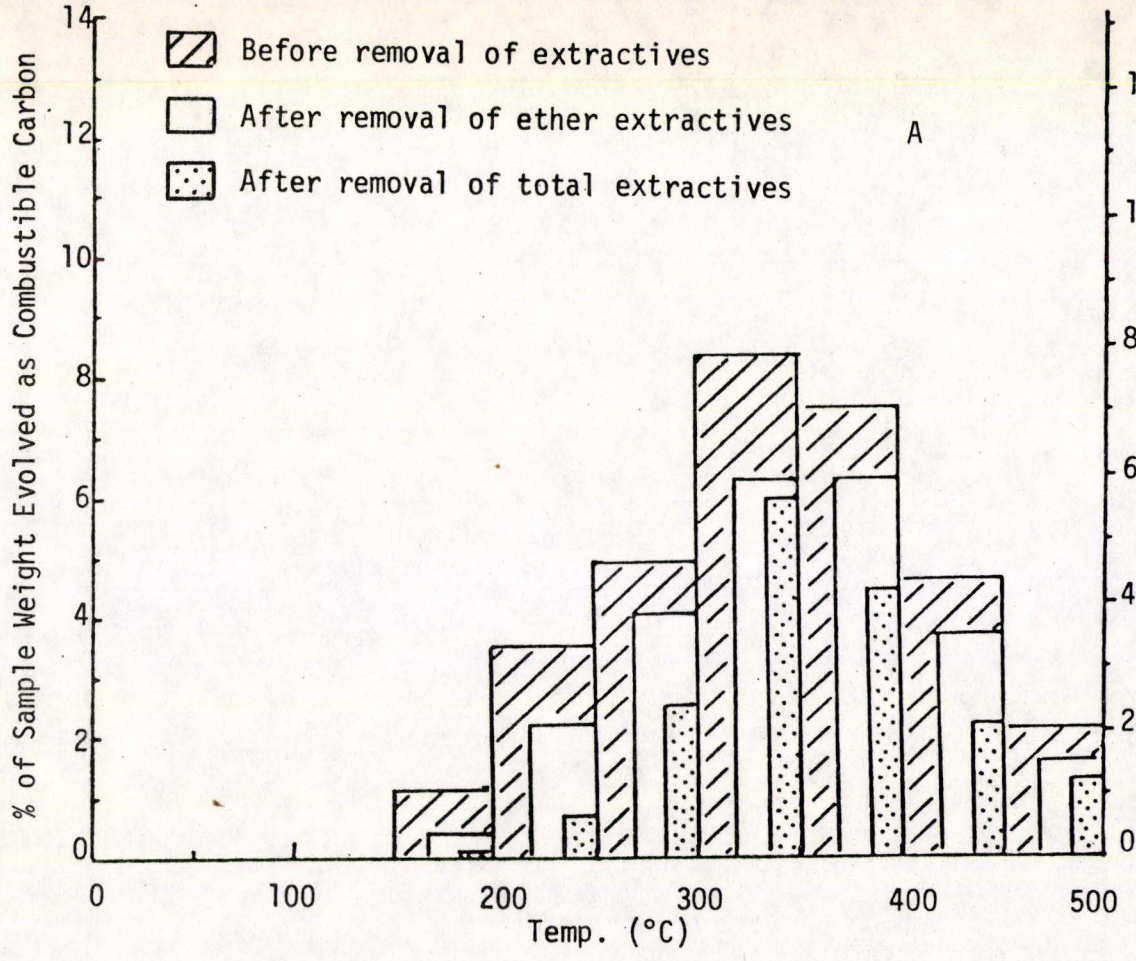


Figure 6. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from manzanita foliage. (A) In temperature intervals and (B) Cumulative.



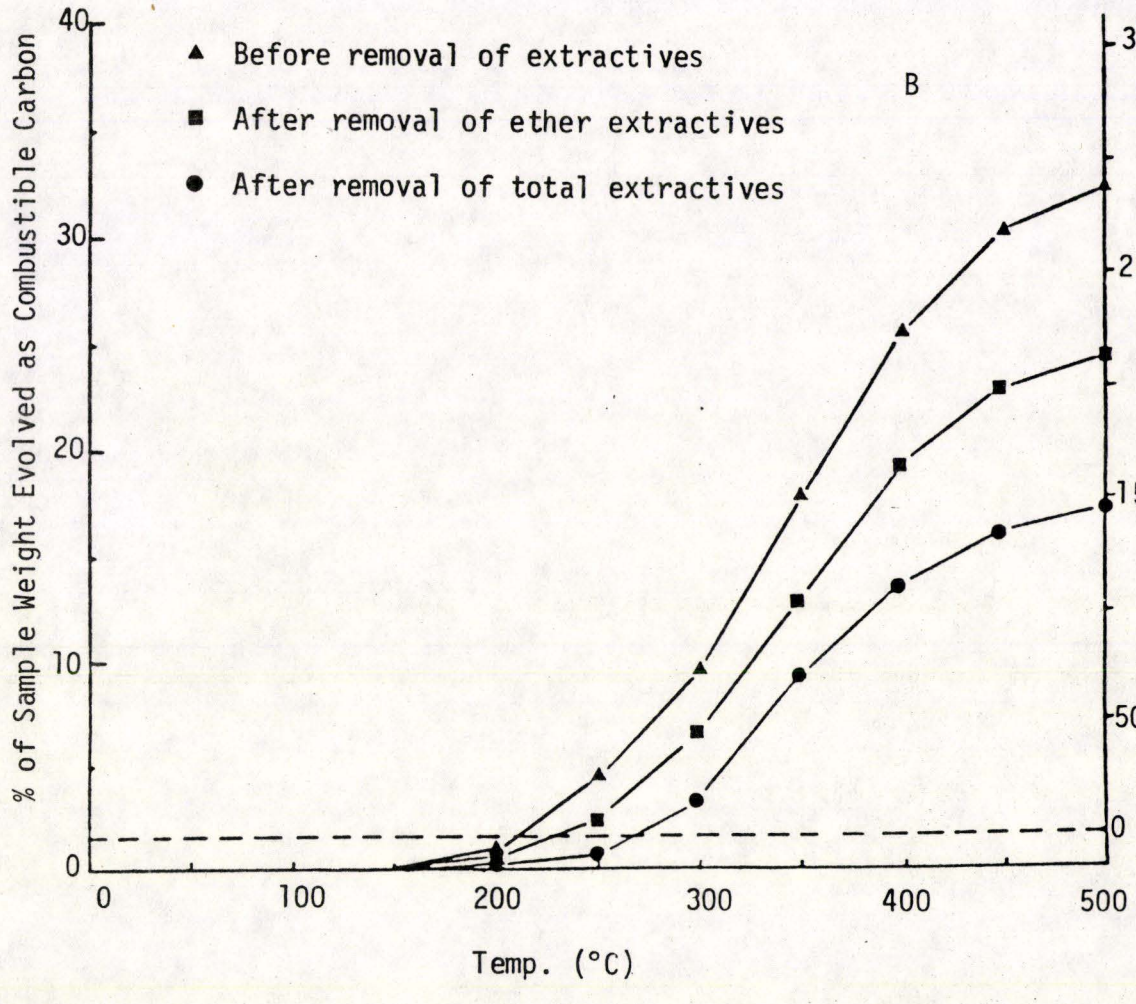
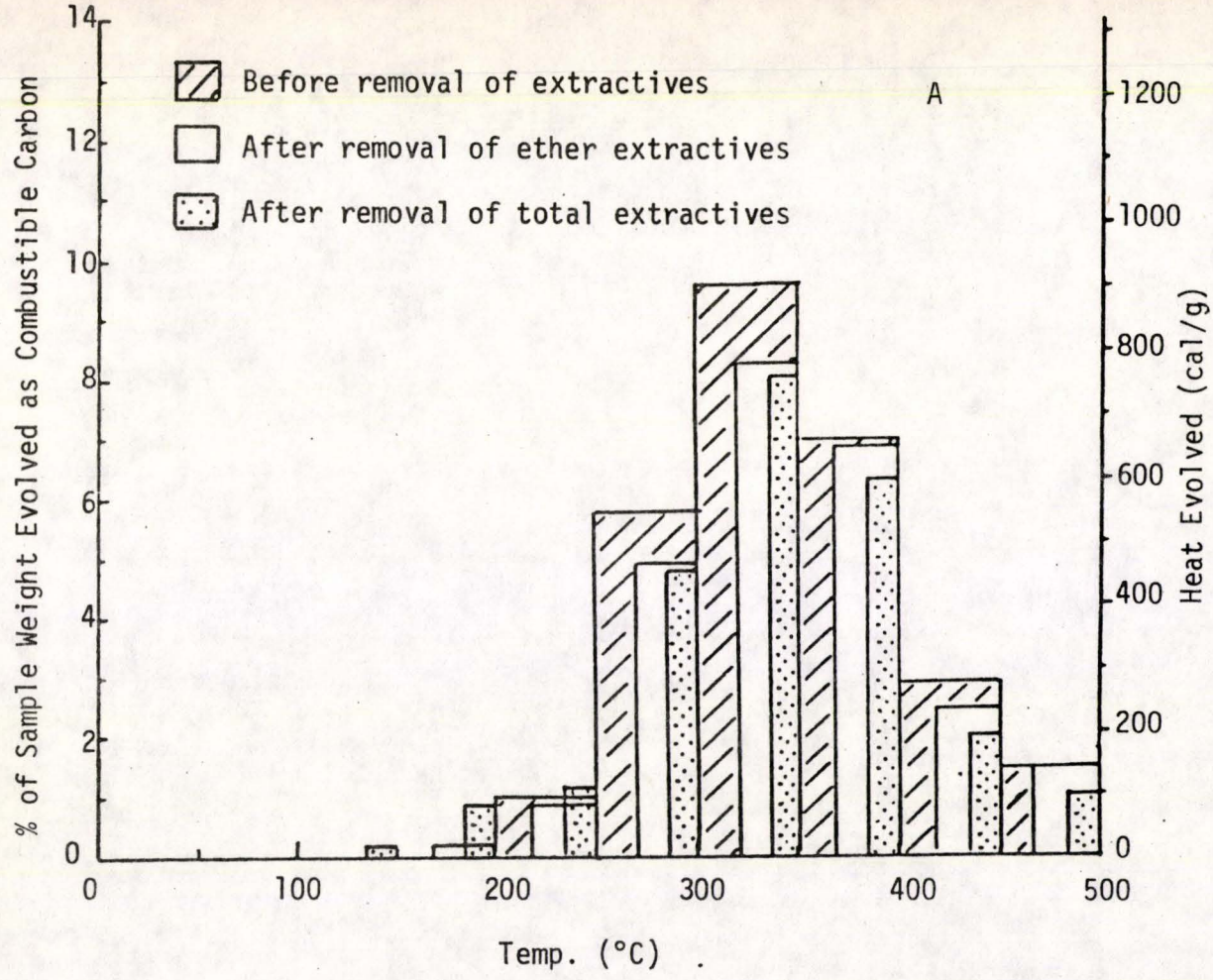


Figure 7. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from ponderosa pine foliage. (A) In temperature intervals and (B) Cumulative.



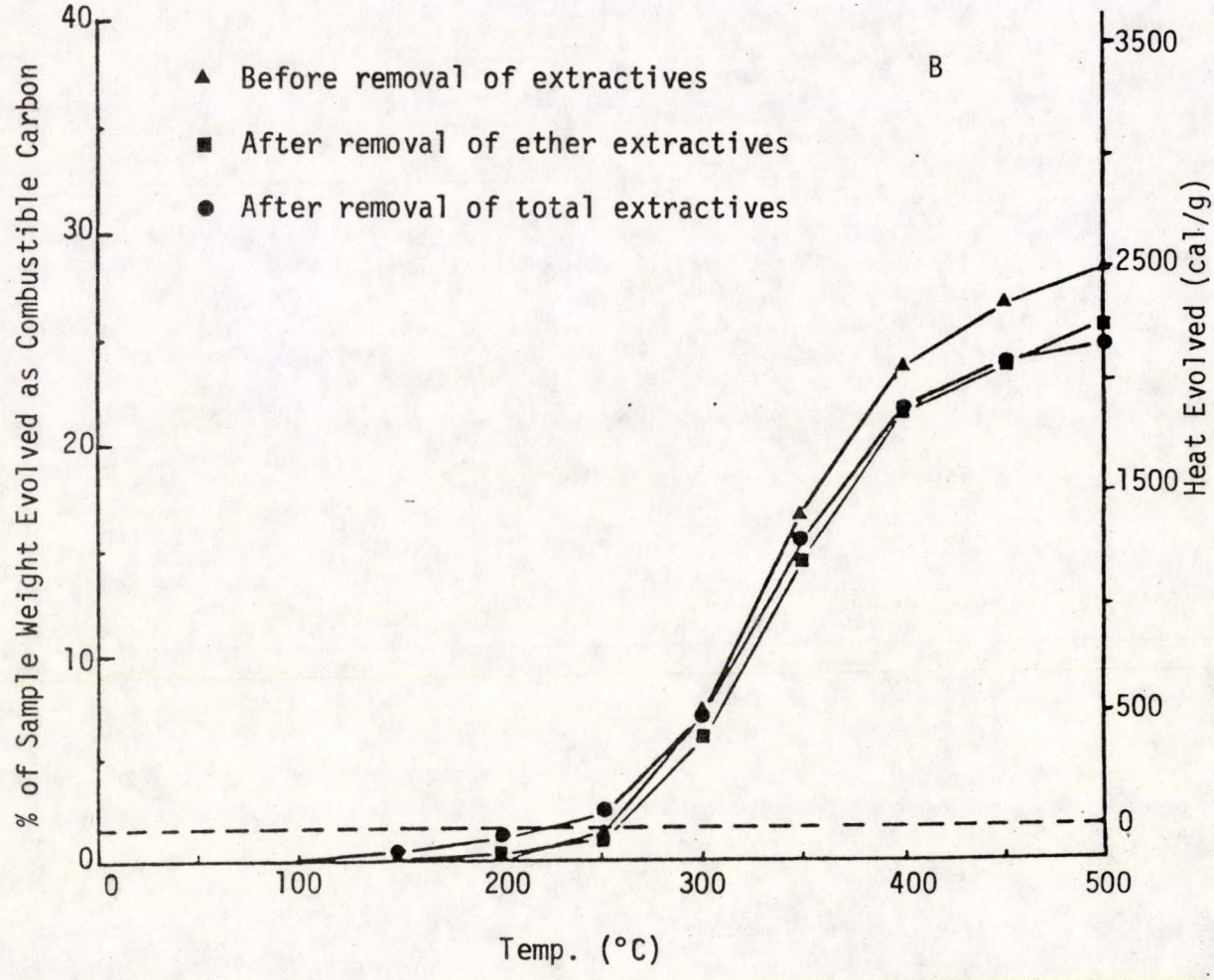


Figure 8. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from sawtooth palmetto foliage. (A) In temperature intervals and (B) Cumulative.

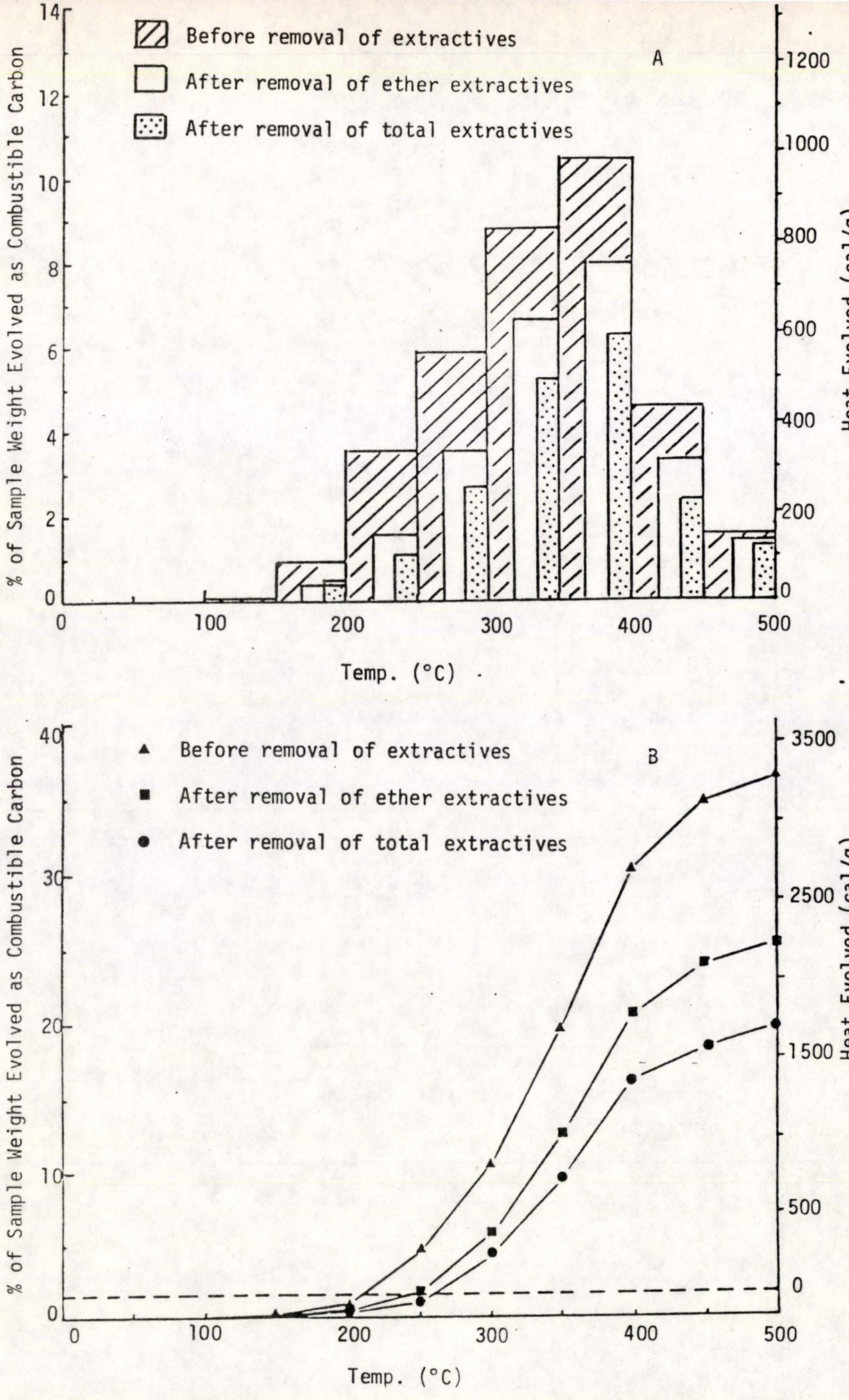


Figure 9. Percent of the original sample weight evolved as combustible carbon, and the heat evolved based on the weight of unextracted sample from slash pine foliage. (A) In temperature intervals and (B) Cumulative.

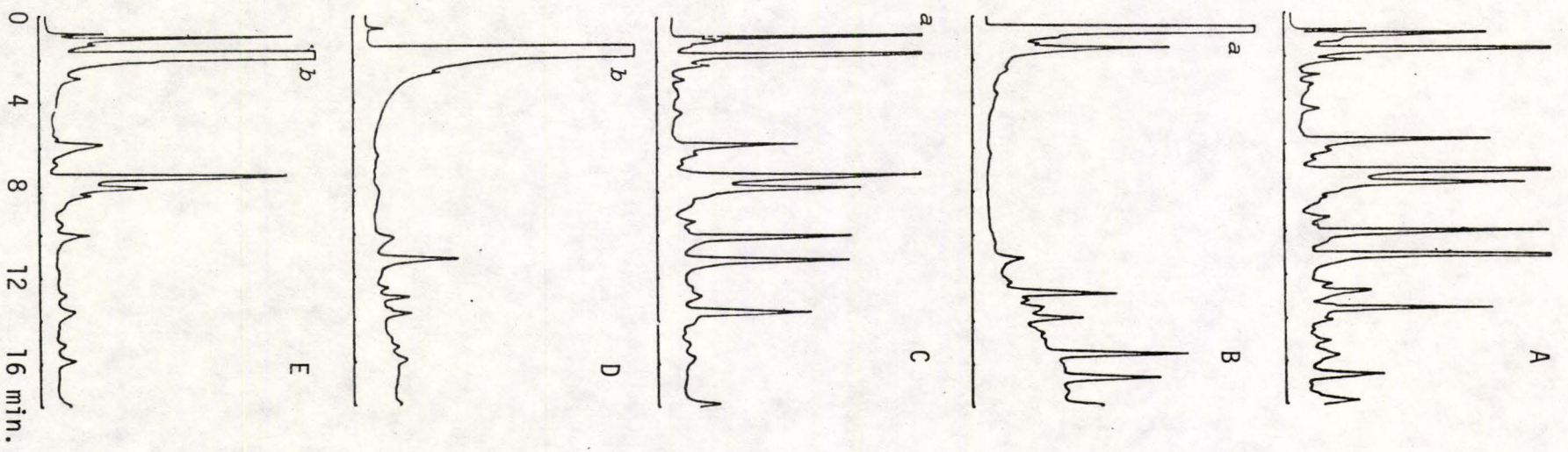


Figure 10. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of aspen foliage. Peak *a* is due to ether solvent and peak *b* is due to benzene and ethanol.

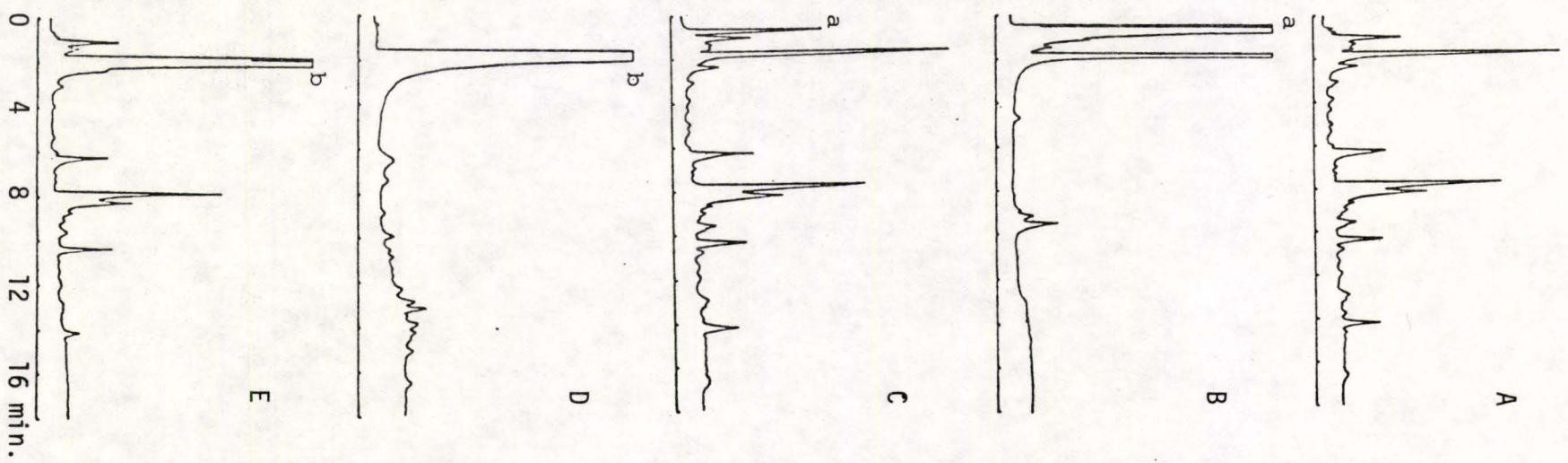


Figure 11. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of chamise foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

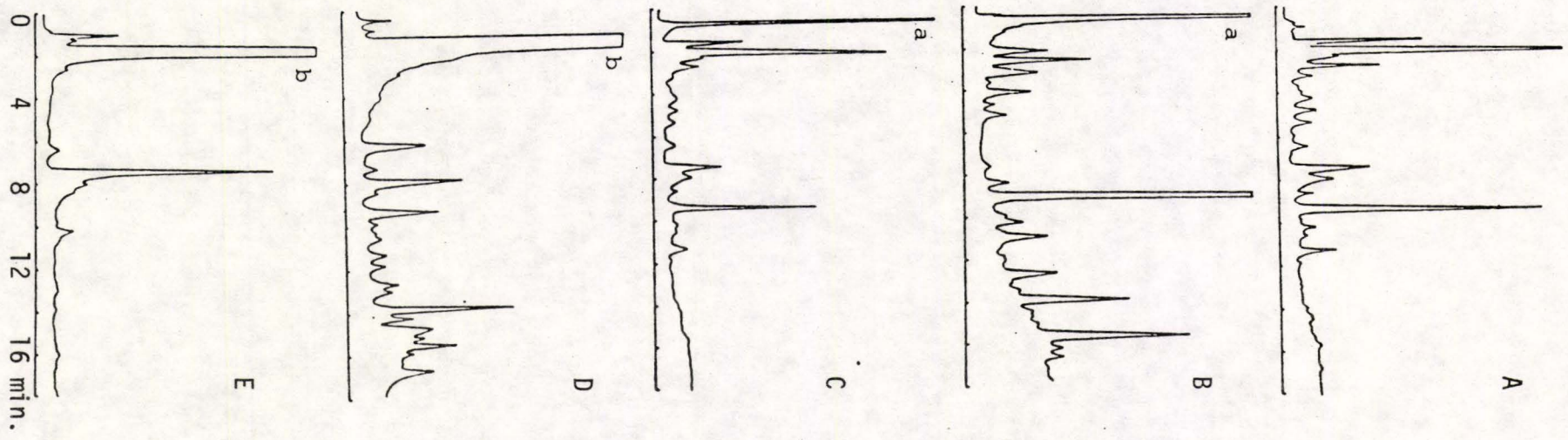


Figure 12. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of Douglas fir foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

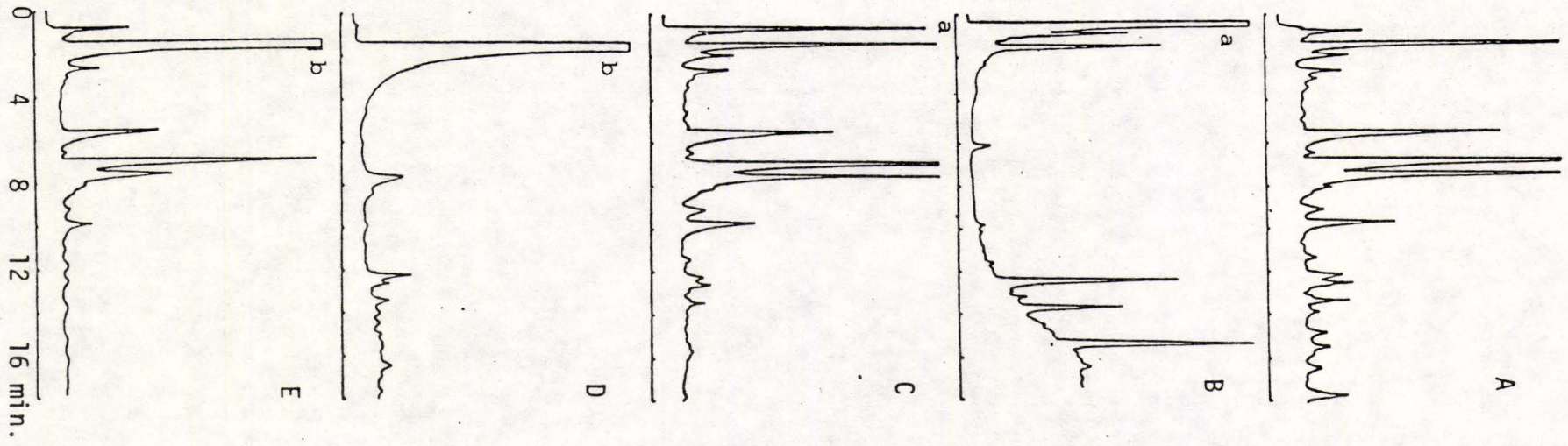


Figure 13. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of gallberry foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

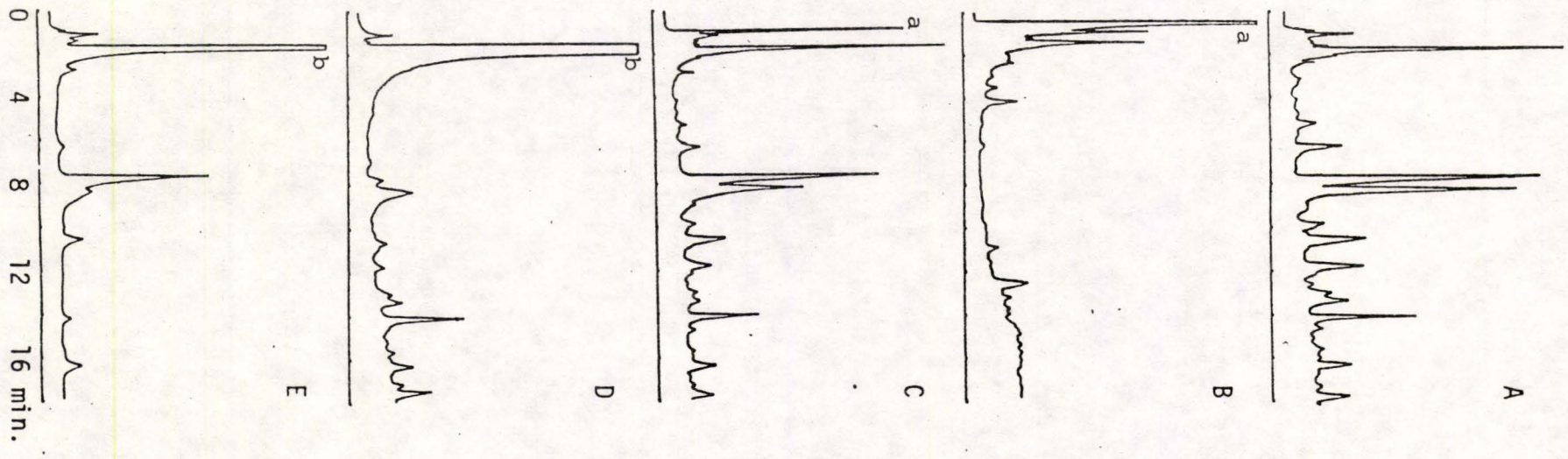


Figure 14. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of lodgepole pine foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

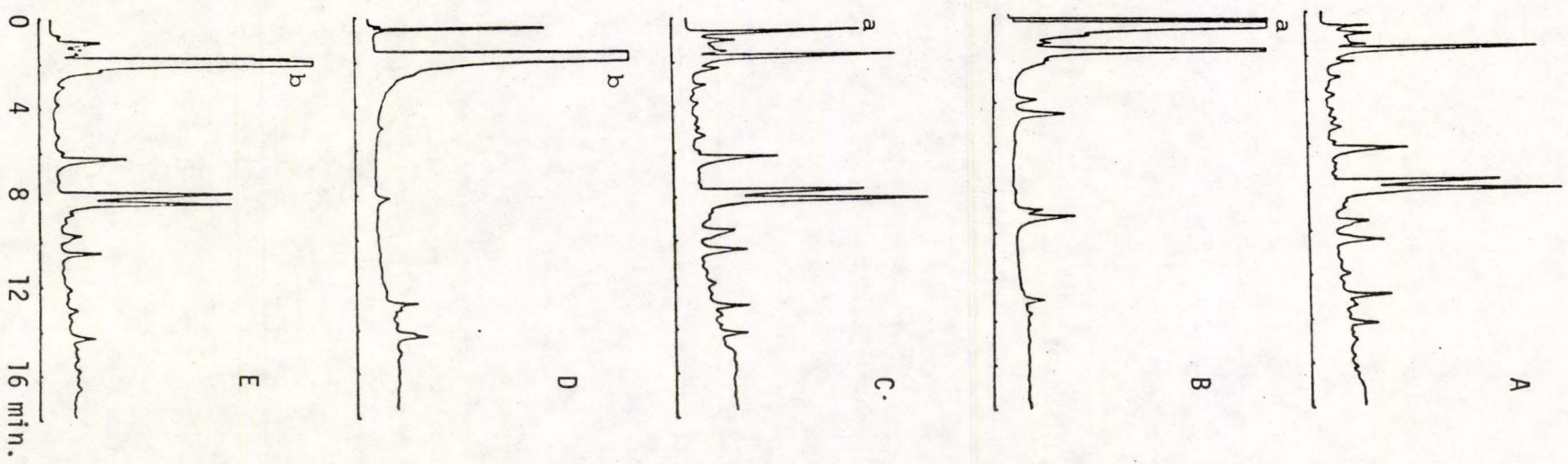


Figure 15. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of manzanita foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

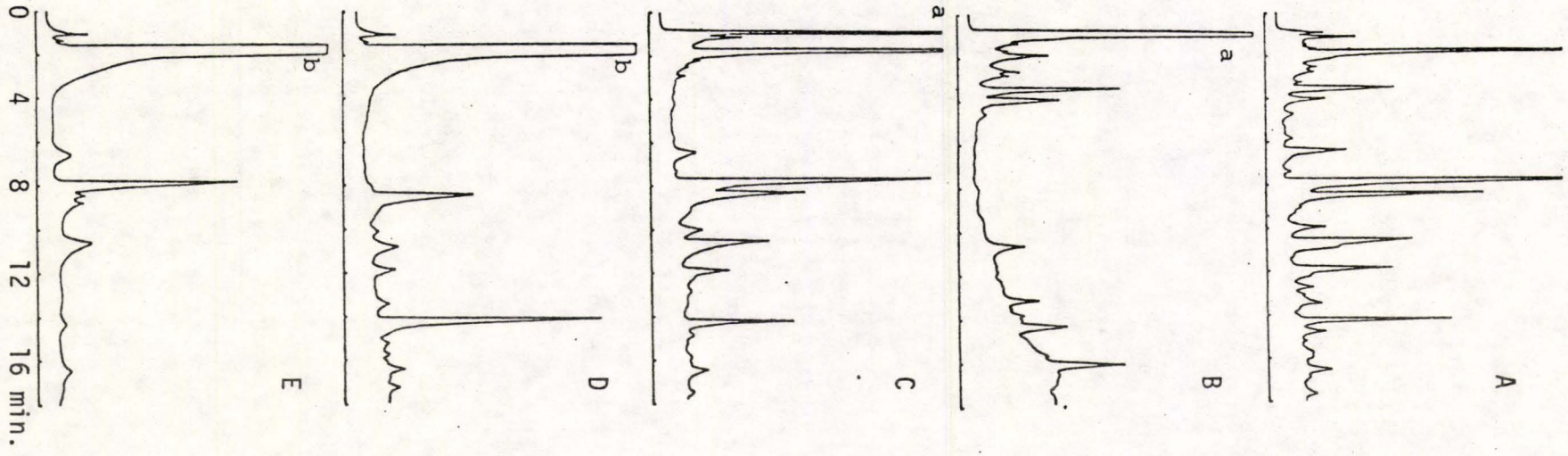


Figure 16. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of ponderosa pine foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

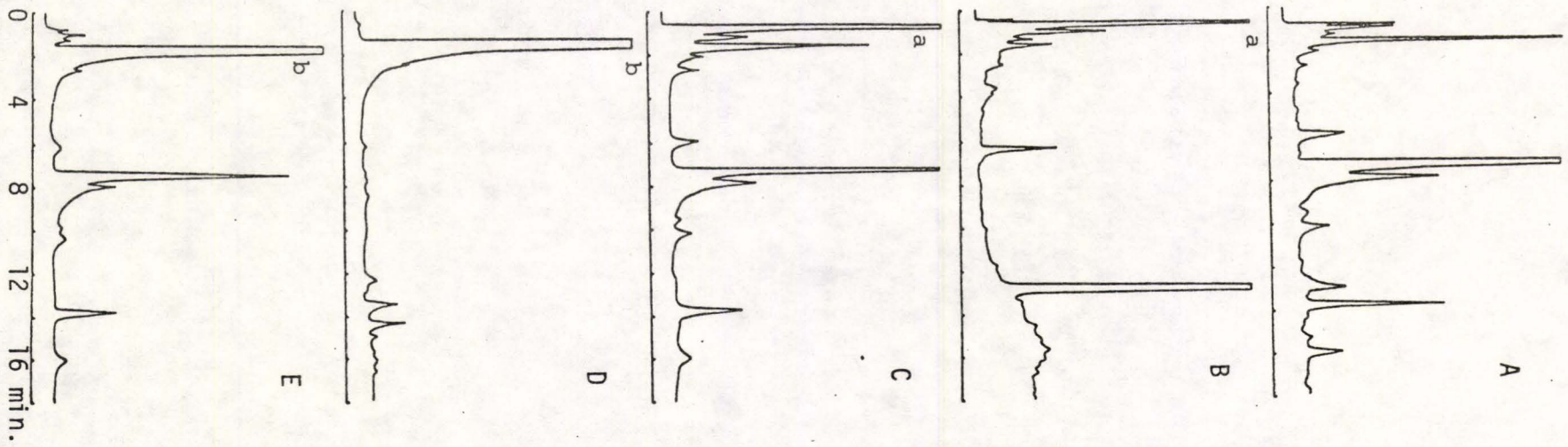


Figure 17. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of sawtooth palmetto foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

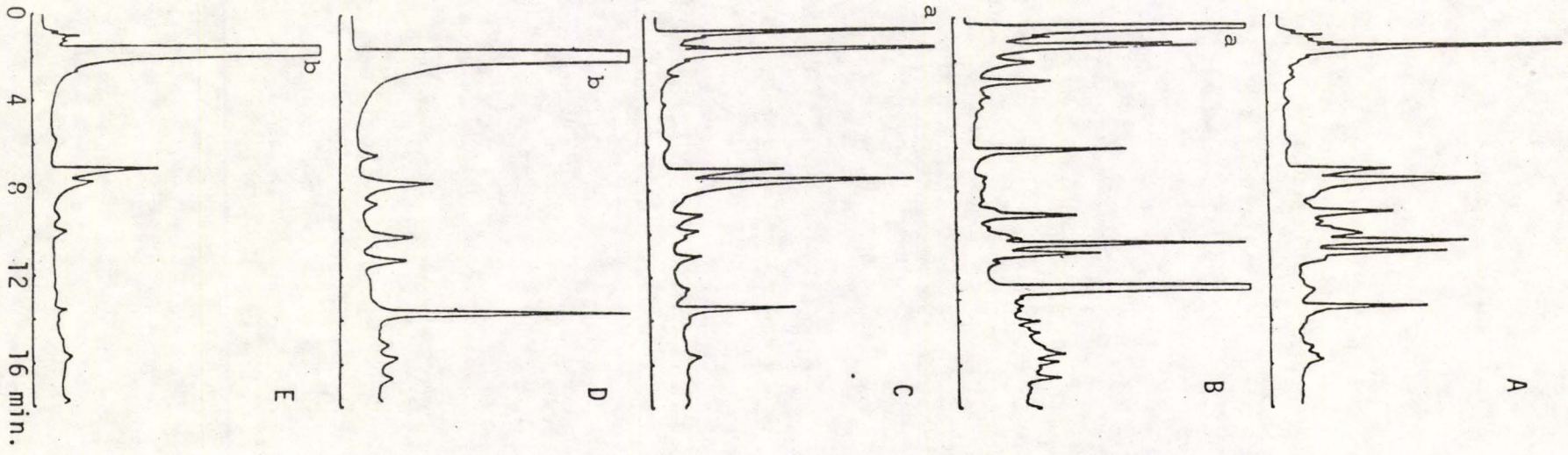


Figure 18. Chromatograms of (A) The volatile products of the unextracted sample heated to 250° (B) The ether extractives (C) The volatile products of the ether-extracted sample heated to 250° (D) The benzene-ethanol extractives and (E) The volatile products of the benzene-ethanol extracted sample heated to 250° of slash pine foliage. Peak a is due to ether solvent and peak b is due to benzene and ethanol.

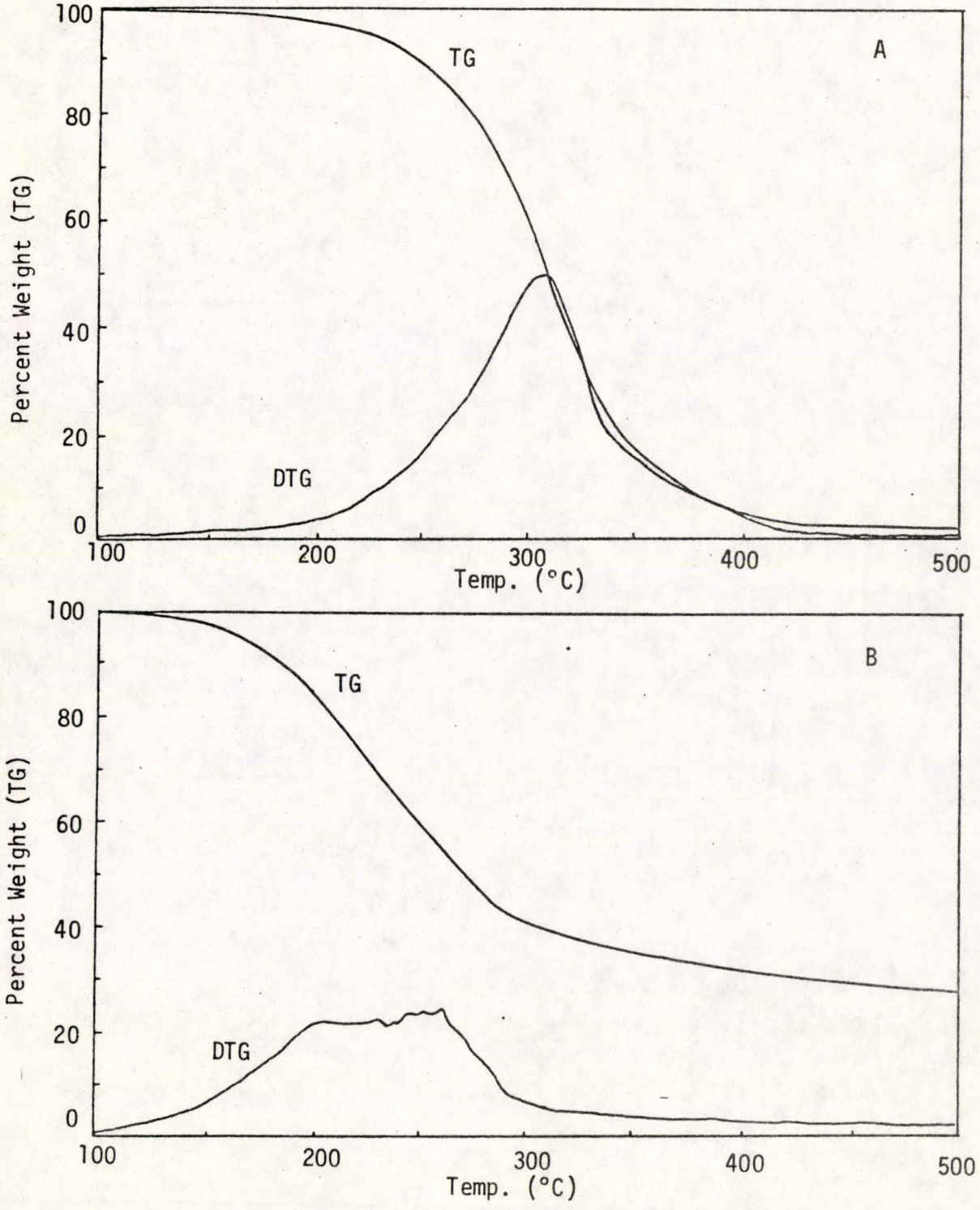


Figure 19. The thermogravimetric analysis of (A) ether extractives and (B) benzene-ethanol extractives of manzanita foliage.

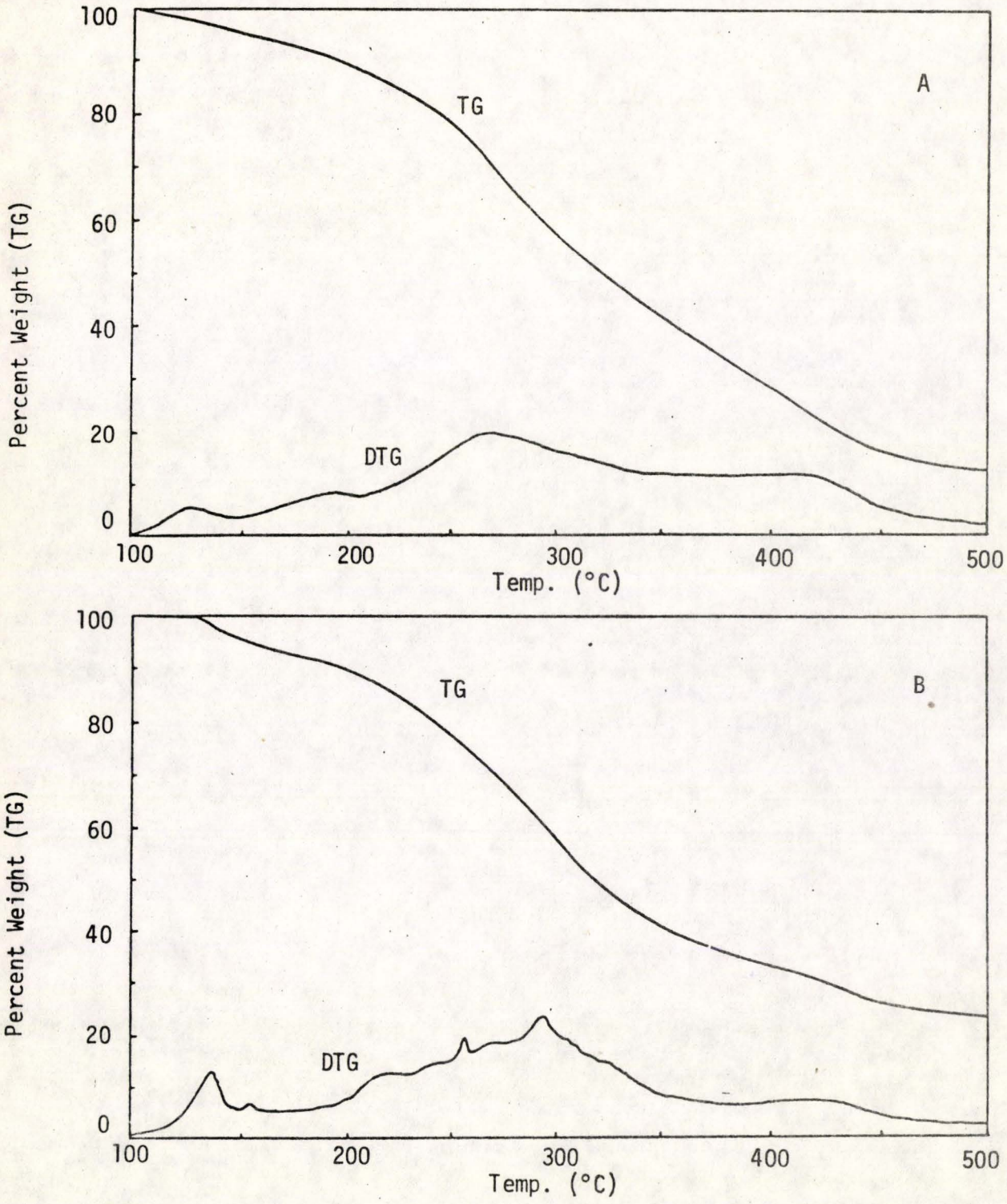


Figure 20. The thermogravimetric analysis of (A) ether extractives and (B) benzene-ethanol extractives of ponderosa pine foliage.